



Electrolyte Solutions: Thermodynamics, Crystallization, Separation methods

Thomsen, Kaj

Link to article, DOI:
[10.11581/dtu:00000073](https://doi.org/10.11581/dtu:00000073)

Publication date:
2009

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Thomsen, K. (2009). *Electrolyte Solutions: Thermodynamics, Crystallization, Separation methods*.
<https://doi.org/10.11581/dtu:00000073>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Electrolyte Solutions: Thermodynamics, Crystallization, Separation methods

2009

Kaj Thomsen, Associate Professor,
DTU Chemical Engineering,
Technical University of Denmark

kth@kt.dtu.dk

List of contents

<u>1</u>	<u>INTRODUCTION.....</u>	<u>5</u>
<u>2</u>	<u>CONCENTRATION UNITS</u>	<u>6</u>
<u>3</u>	<u>IDEAL SOLUTIONS.....</u>	<u>9</u>
3.1	DEFINITION	9
	COLLIGATIVE PROPERTIES	13
<u>4</u>	<u>CHEMICAL POTENTIAL AND ACTIVITY COEFFICIENTS</u>	<u>16</u>
4.1	CHEMICAL POTENTIAL	16
4.2	EXCESS CHEMICAL POTENTIALS FOR REAL SOLUTIONS	16
4.3	THE RATIONAL, UNSYMMETRICAL ACTIVITY COEFFICIENT	17
4.4	THE MOLALITY ACTIVITY COEFFICIENT	18
4.5	THE MOLARITY ACTIVITY COEFFICIENT	19
4.6	THE ACTIVITY OF SPECIES	20
4.7	CHEMICAL POTENTIAL OF A SALT	20
<u>5</u>	<u>MEASUREMENT OF CHEMICAL POTENTIALS IN SALT SOLUTIONS.....</u>	<u>23</u>
5.1	MEASUREMENT OF THE CHEMICAL POTENTIALS OF IONS	23
5.2	THE NERNST EQUATION	24
5.3	THE HARNED CELL	25
5.4	MEASUREMENT OF SOLVENT ACTIVITY	27
5.4.1	FREEZING POINT DEPRESSION AND BOILING POINT ELEVATION MEASUREMENTS	27
5.4.2	VAPOR PRESSURE METHODS	28
5.4.3	ISOPIESTIC MEASUREMENTS.....	29
5.5	OSMOTIC COEFFICIENT	30
5.5.1	THE VALUE OF THE OSMOTIC COEFFICIENT AT INFINITE DILUTION	31
5.6	MEAN ACTIVITY COEFFICIENT FROM OSMOTIC COEFFICIENT	32
5.7	OSMOTIC PRESSURE	33
<u>6</u>	<u>THERMODYNAMIC MODELS FOR ELECTROLYTE SOLUTIONS</u>	<u>35</u>
6.1	ELECTROSTATIC INTERACTIONS	35
6.1.1	DEBYE-HÜCKEL THEORY	35
6.1.2	DEBYE-HÜCKEL EXTENDED LAW	37
6.1.3	DEBYE-HÜCKEL LIMITING LAW	39
6.1.4	THE HÜCKEL EQUATION	40
6.1.5	THE BORN EQUATION.....	42
6.1.6	THE MEAN SPHERICAL APPROXIMATION	44
6.2	EMPIRICAL MODELS FOR INTERMEDIATE/SHORT RANGE INTERACTIONS	46
6.2.1	THE MEISSNER CORRELATION	46
6.2.2	BROMLEY'S METHOD	48
6.2.3	THE PITZER METHOD.....	50

6.3	INTERMEDIATE/SHORT RANGE INTERACTIONS FROM LOCAL COMPOSITION MODELS	54
6.3.1	THE EXTENDED UNIQUAC MODEL	54
6.3.2	THE ELECTROLYTE NRTL MODEL	57
6.4	INTERMEDIATE/SHORT RANGE INTERACTIONS FROM EQUATIONS OF STATE	58
6.4.1	FUGACITY COEFFICIENTS AND ACTIVITY COEFFICIENTS.....	58
6.4.2	THE FÜRST AND RENON EQUATION OF STATE	60
6.4.3	THE WU AND PRAUSNITZ EQUATION OF STATE	60
6.4.4	THE MYERS-SANDLER-WOOD EQUATION OF STATE	61
6.4.5	COMPARATIVE STUDY OF EQUATIONS OF STATE	61
<u>7</u>	<u>EQUILIBRIUM CALCULATIONS</u>	<u>63</u>
7.1	SPECIATION EQUILIBRIUM	63
7.2	SOLID-LIQUID EQUILIBRIUM	64
7.2.1	SATURATION INDEX	65
7.3	VAPOR-LIQUID EQUILIBRIUM	65
7.3.1	HENRY'S CONSTANT	66
7.4	LIQUID-LIQUID EQUILIBRIUM	67
7.5	COMPOSITION DEPENDENCE OF EQUILIBRIUM CONSTANTS	68
7.6	TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANTS	71
7.7	PRESSURE DEPENDENCE OF EQUILIBRIUM CONSTANTS	72
7.7.1	THE PRESSURE DEPENDENCE OF ACTIVITY COEFFICIENTS.....	73
<u>8</u>	<u>THERMAL AND VOLUMETRIC PROPERTIES</u>	<u>75</u>
8.1	PARTIAL AND APPARENT MOLAR PROPERTIES	75
8.2	THERMAL PROPERTIES	75
8.2.1	HEAT OF DILUTION.....	78
8.2.2	HEAT OF SOLUTION	78
8.2.3	MEASUREMENT OF HEATS OF DILUTION AND SOLUTION	80
8.2.4	MEASUREMENT OF HEAT CAPACITY	82
8.3	VOLUMETRIC PROPERTIES	84
<u>9</u>	<u>PHASE DIAGRAMS.....</u>	<u>90</u>
9.1	PHASE RULE AND INVARIANT POINTS	90
9.2	BINARY PHASE DIAGRAM	90
9.3	TERNARY PHASE DIAGRAM	92
9.4	QUATERNARY SYSTEMS	94
<u>10</u>	<u>CRYSTALLIZATION.....</u>	<u>98</u>
10.1	SUPERSATURATION	98
10.2	THE KELVIN EQUATION FOR NUCLEATION	99
10.3	ACTIVATION ENERGY FOR CRYSTAL FORMATION	101
10.4	PRIMARY NUCLEATION RATE	101
<u>11</u>	<u>FRACTIONAL CRYSTALLIZATION.....</u>	<u>102</u>

11.1	PRODUCTION OF KNO_3	105
11.2	OPTIMIZATION OF FRACTIONAL CRYSTALLIZATION PROCESSES	107
11.3	SIMULATION OF K_2SO_4 PRODUCTION PROCESS	108

1 Introduction

Phase equilibria with systems containing electrolytes are of great importance. A few examples may illustrate this: Production of fertilizers and salts is often performed by precipitation of pure solids from multi component ionic solutions. Scaling in heat exchangers is caused by some salts for which the solubility decrease with increasing temperature. Scaling in oil production and in geothermal heat production is caused by some salts for which the solubility decrease with decreasing pressure and decreasing temperature. Solubility of gases in electrolyte solutions is of importance in many pollution abatement processes. The influence of salts on the vapor pressure of aqueous solutions of organic material may be important for the proper choice of a separation process. Salts may even introduce a liquid-liquid phase splitting in aqueous solutions of organic substances.

Electrolytes dissociate into ions when they are dissolved in polar solvents like water or alcohols. A strong electrolyte will dissociate completely while a weak electrolyte will only dissociate partly. The presence of the charged ions causes the electrolyte solution to deviate much more from ideal solution behavior than a non-electrolyte solution does. This is the case even at very low electrolyte concentrations. The reason is that the ions interact with electrostatic forces which are of much longer range than those involved in the interaction of neutral molecules. This effect is stronger the greater the charge on the ions.

For a proper description of electrolyte solutions not only the short range energetic interactions but also the long range electrostatic interactions have to be considered. Another basic difference between electrolyte and non-electrolyte solutions is the constraint of electro-neutrality on electrolyte solutions. Because of this constraint, a system consisting of water and two ions is a binary system: The concentrations of the two ions cannot be chosen independently so the system has two independent components.

Consider salt S that dissociates into ν_C cations C and ν_A anions A with ionic charges Z_C and Z_A .

$$S = \nu_C C^{Z_C} + \nu_A A^{Z_A} \quad (1.1)$$

Table 1.1 Salt dissociation

S	C	Z_C	ν_C	A	Z_A	ν_A
NaCl	Na^+	1	1	Cl^-	-1	1
Na_2SO_4	Na^+	1	2	SO_4^{2-}	-2	1
CaCl_2	Ca^{2+}	2	1	Cl^-	-1	2

The electro-neutrality requirement gives for salt S:

$$\nu_C Z_C + \nu_A Z_A = 0 \quad (1.2)$$

In general the electro-neutrality of a multi component solution containing n_i moles of ion i with the charge Z_i relative to a hydrogen ion can be expressed as:

$$\sum_i n_i Z_i = 0 \quad (1.3)$$

Sodium chloride is often described as a 1-1 salt, sodium sulfate as a 1-2 salt, calcium chloride as a 2-1 salt, and calcium sulfate as a 2-2 salt, based on the values of the ionic charges.

2 Concentration units

In the following, it is assumed that the electrolytes are dissolved in water. Water is considered to be the only solvent, electrolytes and non-electrolytes are considered to be solutes. In a solution containing water, salts, and methanol, water is considered to be the solvent. The ions and methanol are considered to be solutes. As it will be shown, this approach has significant advantages when performing solid-liquid equilibrium calculations and liquid-liquid equilibrium calculations for solutions containing non-electrolytes in addition to electrolytes. In another approach often seen in the literature, mixtures of water and certain non-electrolytes such as organic solvents are considered to be separate species, “mixed solvents” or pseudo solvents, while other non-electrolytes and electrolytes are considered to be solutes.

For the description of electrolyte solutions the most common concentration unit is the molality. The molality unit is very often used in the presentation of experimental data, while the mole fraction unit most often is used in thermodynamic models for electrolytes. The molarity unit is also often used, but is dependent on temperature and to a certain extent also on pressure. It is not a practical unit because the density needs to be known in order to convert molarity units to molality units or mole fraction units.

The molality m_i of an ion i is the number of moles n_i , of the ion per kg water in the liquid phase:

$$m_i = \frac{n_i}{n_w M_w} \text{ mol/kg water} \quad (2.1)$$

The amount of water in the solution is here calculated as the product of n_w , the number of moles of water and M_w , the molar mass of water in kg/mol.

The molarity c_i of an ion i is the number of moles of the ion per liter solution:

$$c_i = \frac{n_i}{V_{\text{solution}}} \text{ mol/liter solution} \quad (2.2)$$

The volume of the solution, V_{solution} , is related to its mass and its density:

$$d_{\text{solution}} = \frac{n_w M_w + \sum_{\text{ions}} n_i M_i}{V_{\text{solution}}} \quad (2.3)$$

If the density of the solution d_{solution} is given in kg/liter and the molar masses of water and ions are given in kg/mol, the volume of the solution will be calculated in liter.

From equation (2.1) it can be seen that the molality concentration unit is only dependent on the amount of the relevant solute and the amount of solvent. The mole fraction unit and the molarity units on the other hand are also dependent on the amount of other solutes present. In addition, the molarity unit is also dependent on temperature and pressure because the density of the solution depends on temperature and pressure.

Example 2.1: A solution containing 6 mol of sodium chloride and one kg of water is a 6 molal solution of sodium chloride. The molality of the sodium ion in the solution is 6. The molar mass of water is 18.02 gram/mol, and the number of mol water in one kg water can therefore be calculated as 1000/18.02. The molality of the chloride ion in the solution is also 6. The mole fraction of the sodium ion is

$$x_{Na^+} = \frac{n_{Na^+}}{n_{Na^+} + n_{Cl^-} + n_{H_2O}} = \frac{6}{6 + 6 + 1000/18.02} = 0.0889$$

The mole fraction of the chloride ion is also 0.0889. The mole fraction of water is

$$x_w = \frac{1000/18.02}{6 + 6 + 1000/18.02} = 0.8222$$

Sometimes the composition of an electrolyte solution is given in terms of the amounts of water and salts instead of water and ions. If this approach is used, the composition of the same solution can be described by the mole fraction of sodium chloride:

$$x_{NaCl} = \frac{n_{NaCl}}{n_{NaCl} + n_{H_2O}} = \frac{6}{6 + 1000/18.02} = 0.0975$$

The mole fraction of water is $1 - 0.0975 = 0.9025$ when this approach is used.

The density of this solution is 1.1942 kg/liter at 25 °C and 1 bar. The volume of the solution can be calculated from equation (2.3):

$$V_{solution} = \frac{n_w M_w + n_{Na^+} M_{Na^+} + n_{Cl^-} M_{Cl^-}}{1.1942} = \frac{1.000 + 6.0 \cdot 0.02299 + 6.0 \cdot 0.035453}{1.1942} = 1.1310 \text{ liter}$$

The molarity of the sodium ion, the chloride ion and of sodium chloride in the solution is:

$$c_{Na^+} = c_{Cl^-} = c_{NaCl} = \frac{6}{1.1310} = 5.305 \text{ mol/liter}$$

At 100 °C and 1 bar, the density of the same sodium chloride solution is 1.1490 kg/liter. The volume of the solution is 1.1755 liter and the molarity of sodium chloride is 5.104 mol/liter.

For a salt S the molality is:

$$m_S = \frac{n_S}{n_w M_w} \quad (2.4)$$

If the salt dissociates into ν_C cations and ν_A anions the molality of the cation C is:

$$m_C = \frac{\nu_C n_S}{n_w M_w} = \nu_C m_S \quad (2.5)$$

The molality of the anion A is:

$$m_A = \frac{\nu_A n_S}{n_w M_w} = \nu_A m_S \quad (2.6)$$

The molality m_S of the salt can therefore be expressed either in terms of the cation molality or in terms of the anion molality:

$$m_S = \frac{m_C}{\nu_C} \quad \text{or} \quad m_S = \frac{m_A}{\nu_A} \quad (2.7)$$

Most thermodynamic models use the traditional mole fraction scale:

$$x_i = \frac{n_i}{\sum n_j} \quad (2.8)$$

The summation in the denominator is over all solute and solvent species. A relation between the molality unit and the mole fraction unit can be derived as follows:

$$x_i = \frac{n_i}{\sum n_j} = \frac{n_i}{\sum n_j} \frac{n_w M_w}{n_w M_w} = m_i x_w M_w \quad (2.9)$$

M_w is the molar mass of water given in kg/mol.

The molarity unit is related to the mole fraction unit by:

$$x_i = \frac{n_i}{\sum n_j} = \frac{n_i}{\sum n_j} \frac{V_{\text{solution}}}{V_{\text{solution}}} = \frac{c_i V_{\text{solution}}}{\sum n_j} \quad (2.10)$$

A large number of different concentration units are used to present experimental data for electrolytes. These include:

1. Mass percent
2. molality
3. Mole fraction (water, ions, and non electrolytes)
4. Mole fraction (water, salts, and non electrolytes)
5. Mass of salt per mass of H₂O
6. Mass of salt per volume solution
7. Mole salt per volume of solution
8. Mole salt per mass of solution
9. Jänecke coordinates (Charge fraction + gram H₂O per mole salts)
10. Mass percent solvent (salt free) + molality of salt
11. Mass percent solvent(salt free) + mass of salt per mass of mixed solvent
12. Mole percent solvent(salt free) + molality salt

One reason why molality is a popular unit for salt solutions is that the concentrations in molality units give practical numbers, often between 0 and 20 for most salts, while the concentrations in mole fraction units are very small as indicated in figure 2.1: The figures show the phase diagram of the ternary system NaCl-KCl-H₂O using these two different concentration units. The lines in the phase diagrams mark concentrations saturated with either NaCl or KCl. At 25°C, the solubility of NaCl is 6.15 mol/kg water, 0.0997 salt mole fraction, or 26.4 mass percent. The corresponding numbers for KCl are 4.79 mol/kg water, 0.0795 salt mole fraction, or 20.7 mass percent.

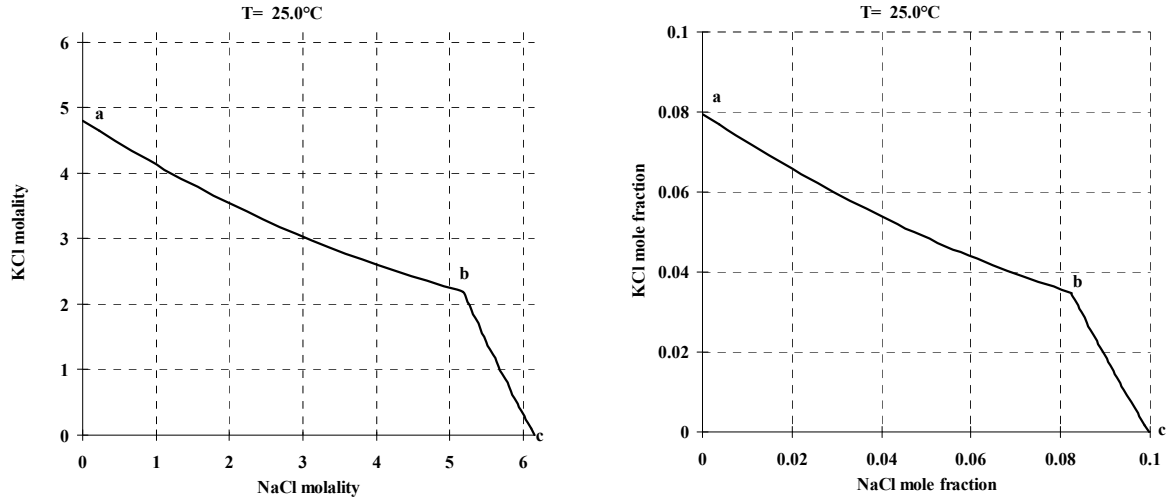


Figure 2.1: Phase diagram for the NaCl-KCl-H₂O system using molality as concentration unit (left) and salt mole fraction (right). The phase diagram consists of two curves. On the curve a - b solid potassium chloride is in equilibrium with saturated solutions. On b - c solid sodium chloride is in equilibrium with saturated solutions. In the point b both solid salts are in equilibrium with a saturated solution.

3 Ideal solutions

3.1 Definition

An ideal solution can be defined as a solution in which the molar Gibbs energy of species i is calculated as:

$$G_i^{id} = G_i^0 + RT \ln x_i \quad (3.1)$$

R is the gas constant, T is the absolute temperature in Kelvin, and x_i is the mole fraction of component i . Based on the definition of the ideal solution, the properties of real solutions can be calculated by the sum of two terms: an ideal term and an excess term. Equation (3.1) defines the ideal term of the Gibbs energy and is therefore given the superscript *id*. G_i^0 is the molar standard state Gibbs energy and is a function of temperature and pressure.

If there is only one component, the mole fraction x_i of component i is equal to one. The term $RT \ln x_i$ then becomes zero, and the Gibbs energy of i is equal to the standard state Gibbs energy of i at the temperature and pressure. Therefore this standard state is often called the “pure component standard state”.

An alternative definition of the ideal solution is based on the molality scale:

$$G_i^{id,m} = G_i^m + RT \ln m_i \quad (3.2)$$

The ideal solution Gibbs energy calculated from equation (3.1) is different from the one calculated from equation (3.2). The latter is therefore marked with superscript *m*. G_i^m is the value of the molar standard state Gibbs energy on the molality scale and is a function of temperature and pressure.

The entropy of component i is related to the Gibbs energy through the fundamental thermodynamic relation:

$$S_i = - \left[\frac{\partial G_i}{\partial T} \right]_{P,x} \quad (3.3)$$

The entropy of component i in an ideal solution can be calculated from equation (3.1) using the relation in (3.2):

$$S_i^{id} = - \left[\frac{\partial G_i^{id}}{\partial T} \right] = - \left[\frac{\partial G_i^0}{\partial T} \right] - R \ln x_i = S_i^0 - R \ln x_i \quad (3.4)$$

S_i^0 is the molar standard state entropy of component i and is a function of temperature and pressure.

Through the fundamental thermodynamic relation $G_i = H_i - TS_i$, the enthalpy of component i in an ideal solution can be calculated from equations (3.1) and (3.3):

$$H_i^{id} = G_i + TS_i = G_i^0 + RT \ln x_i + TS_i^0 - RT \ln x_i = G_i^0 + TS_i^0 = H_i^0 \quad (3.5)$$

H_i^0 is the molar standard state enthalpy of component i and is a function of temperature and pressure. The Gibbs energy and the entropy of a component in an ideal solution both depend on the composition of the solution according to equation (3.1) and (3.3). According to equation (3.5), the enthalpy of a component in an ideal solution is not dependent on the composition.

Example 3.1

We will calculate the phase diagram from Figure 2.1 assuming ideal solution behavior. The phase diagram consists of two equilibrium curves. On one curve solid potassium chloride is in equilibrium with a saturated solution. On the other curve solid sodium chloride is in equilibrium with a saturated solution. The two equilibria can be expressed as:



The brackets (s) indicate solid, crystalline phase, the brackets (aq) indicate solutes in aqueous solution.

Equilibrium is attained when there is no Gibbs energy change for a pair of ions that choose to go from the crystalline phase to the aqueous phase or vice versa.

The equilibria we consider in this example are heterogeneous, involving two solid phases and a liquid phase. The solid phases are pure, homogeneous phases, not mixtures. Even in point b in Figure 2.1 where two solid salts are in equilibrium with the same liquid, the two solid salts will form crystals of pure NaCl and of pure KCl. In other systems, for example mixtures of ammonium and potassium salts, there is a tendency to form mixed crystals, solid solutions, due to the similarity of the two cations.

The Gibbs energy of the pure solid salts can be found in thermodynamic tables. Also the Gibbs energy of the aqueous ions can be found in such tables. Table 5.2 contains the values necessary to calculate the phase diagram in Figure 2.1.

The Gibbs energy of each component in the molality based ideal solution can be expressed using equation (3.2):

$$\begin{aligned}
G_{K^+(aq)}^{id,m} &= \Delta_f G_{K^+(aq)}^m + RT \ln m_{K^+} \\
G_{Cl^-(aq)}^{id,m} &= \Delta_f G_{Cl^-(aq)}^m + RT \ln m_{Cl^-} \\
G_{KCl(s)} &= \Delta_f G_{KCl(s)} \\
G_{NaCl(s)} &= \Delta_f G_{NaCl(s)}
\end{aligned} \tag{3.7}$$

All the Gibbs energies used are Gibbs energies of *formation* as indicated by the subscript *f*. The Gibbs energies of formation refer to the same standard state: The natural state of the elements at 25°C and 1 bar. The values therefore allow us to calculate the Gibbs energy change by reactions among these compounds.

The condition for equilibrium of potassium and chloride ions with solid potassium chloride is that the Gibbs energy is identical in the two phases, which can be expressed as:

$$G_{K^+(aq)}^{id,m} + G_{Cl^-(aq)}^{id,m} = G_{KCl(s)} \tag{3.8}$$

or

$$\Delta_f G_{K^+(aq)}^m + RT \ln m_{K^+} + \Delta_f G_{Cl^-(aq)}^m + RT \ln m_{Cl^-} = \Delta_f G_{KCl(s)}^m$$

A corresponding expression for sodium chloride could also be written. By inserting numbers from Table 5.2, the following expression is obtained for potassium chloride:

$$-283270 + RT \ln m_{K^+} - 131228 + RT \ln m_{Cl^-} = -409140$$

The equation can be modified to (3.9)

$$m_{K^+} m_{Cl^-} = \exp\left(\frac{5358}{RT}\right) = \exp\left(\frac{5358}{8.314 \cdot 298.15}\right) = 8.6843$$

By a similar method the corresponding equation for the equilibrium of sodium chloride can be derived as:

$$m_{Na^+} m_{Cl^-} = \exp\left(\frac{8995}{RT}\right) = 37.6655 \tag{3.10}$$

The curve for KCl solubility can now be calculated at fixed concentrations of NaCl by using equation (3.9). Because the NaCl concentration is fixed, the molality of Cl^- can be calculated as the molality of NaCl plus the molality of K^+ . The molality of K^+ therefore is the only unknown. The curve for NaCl solubility can be calculated at fixed concentrations of KCl by using equation (3.10) in a similar manner. The point b from Figure 2.1 can be calculated by solving equation (3.9) and (3.10) simultaneously.

The result of the calculation is shown in Figure 3.1. The calculated solubility of sodium chloride is very close to the

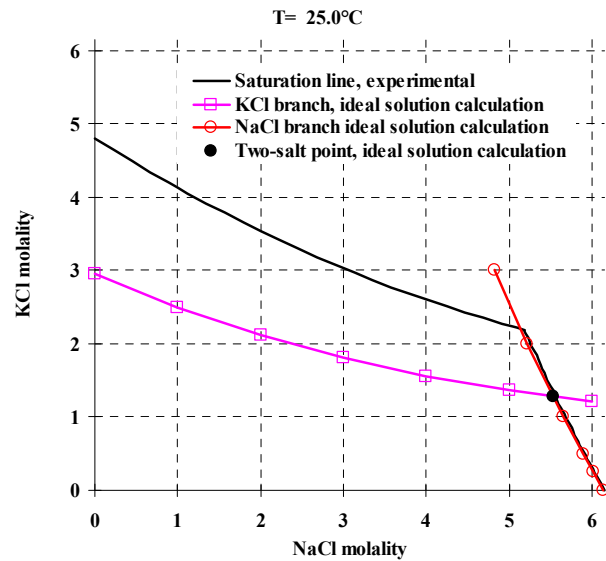


Figure 3.1: Phase diagram for the KCl-NaCl-H₂O system calculated assuming ideal solution behavior.

Table 3.1: Calculation of phase diagram for the KCl-NaCl-H₂O system assuming ideal solution behavior. Concentrations are in molality (mol/kg water).

m_{NaCl} (fixed)	m_{Cl^-}	m_{K^+}	Solid Phase
0.0000	2.9469	2.9469	KCl
1.0000	3.4890	2.4890	KCl
2.0000	4.1120	2.1120	KCl
3.0000	4.8067	1.8067	KCl
4.0000	5.5615	1.5615	KCl
5.0000	6.3645	1.3645	KCl
6.0000	7.2053	1.2053	KCl
m_{KCl} (fixed)	m_{Cl^-}	m_{Na^+}	
0.0000	6.1372	6.1372	NaCl
0.2500	6.2635	6.0135	NaCl
0.5000	6.3923	5.8923	NaCl
1.0000	6.6576	5.6576	NaCl
2.0000	7.2182	5.2182	NaCl
3.0000	7.8179	4.8179	NaCl
m_{Na^+}	m_{K^+}	m_{Cl^-}	
5.5325	1.2756	6.8081	NaCl+KCl

actual solubility of sodium chloride. For potassium chloride on the other hand, the calculated solubility is much lower than the actual solubility of potassium chloride. This indicates that one of these apparently similar salts has ideal solution behavior while the other deviates strongly from ideal behavior. This is a coincidence caused by the fact that the mean molal activity coefficient of sodium chloride has values near 1 at concentrations near saturation of NaCl at room temperature.

Obviously, the ideal solution assumption gives results that deviate significantly from the experimental value of the solubility in this system. In order to make this kind of calculations correct, it is very important to use a thermodynamic model that takes the deviation from ideality into account.

Exercise 3.1

In Example 3.1, the solid-liquid phase diagram of the ternary system KCl – NaCl – H₂O system at 25°C was calculated, assuming ideal solution behavior and using molality as concentration scale. Derive the corresponding equations necessary for calculating the same phase diagram using mole fraction as the concentration scale, and calculate the phase diagram.

The Gibbs energies of formation for the ions based on the mole fraction scale are given in table 3.2.

Table 3.2: Standard state Gibbs energy of formation of ions at 25°C. The values are based on the mole fraction concentration scale.

	Na ⁺	K ⁺	Cl ⁻
$\Delta_f G$ kJ/mol	-251.949	-273.314	-121.272

Colligative properties

Colligative properties are properties that according to physical chemistry textbooks are independent of the type of species in the solution but are dependent on the amount of species. As it will be shown here, these colligative properties are not independent of the type of species. On the contrary, they are strongly depending on the type of species. The colligative properties are freezing point depression and boiling point elevation. Vapor pressure lowering and osmotic pressure are usually mentioned separately as colligative properties but these two latter properties are so closely related to the boiling point elevation that they don't need to be discussed separately.

In a freezing point depression experiment, the temperature at which solid solvent (ice) is in equilibrium with a solution is determined. This temperature is lower than the freezing point of pure water. In a boiling point elevation experiment, the temperature at which solvent vapor (steam) is in equilibrium with the solution is determined. At atmospheric pressure, this boiling point is higher than the normal boiling point of pure water.

These phenomena can be understood by considering equation (3.1), and (3.2). According to these equations, the Gibbs energy of an ideal solution depends on the composition of the solution in addition to temperature and pressure. Ice and steam are two pure phases. The Gibbs energies of pure phases depend only on temperature and pressure. At equilibrium between solution and ice or solution and steam, the Gibbs energy of water in solution is identical to the Gibbs energy of ice or that of steam respectively. By varying the composition, it will therefore be possible to find a range of temperatures and pressures at which there is equilibrium between an ideal solution and the pure phases, ice and steam respectively.

The equilibria between solutions and pure phases can be expressed as:

$$\Delta_f G_w^0(T, P) + RT \ln x_w = \Delta_f G_{ice}^0(T, P) \quad \text{for freezing point depression}$$

and (3.11)

$$\Delta_f G_w^0(T, P) + RT \ln x_w = \Delta_f G_{steam}^0(T, P) \quad \text{for boiling point elevation}$$

The left hand sides of the equations (3.11) express the Gibbs energies of ideal solutions as functions of composition, temperature and pressure. The right hand sides of the expressions give the Gibbs energies of the pure phases as functions of temperature and pressure. By varying the water mole fractions it is possible to determine a range of temperatures and pressures at which these equilibria can be established.

The expression for the equilibrium between aqueous solution and ice, equation (3.11) is plotted in figure 3.2 together with experimentally measured freezing point depressions. The pressure was held constant at 1 bar. The freezing point temperatures were calculated at a number of water mole fractions, using equation (3.11). The water mole fractions were converted to mol solute per kg water. The experimental data marked in Figure 3.2 show a significant difference between real electrolyte solutions and ideal solution behavior. The data also show a significant difference between the freezing point depressions caused by different electrolytes.

Apparently, sodium chloride solutions are closer to ideal solution behavior than magnesium chloride solutions are. A solution containing 5.08 moles NaCl per kg water freezes at -21.7°C. Assuming full dissociation such a solution contains 10.16 mol solutes (Na^+ and Cl^- ions) per kg water. This solution is called a eutectic solution because it is the sodium chloride solution with the lowest possible freezing point. A eutectic solution of magnesium chloride

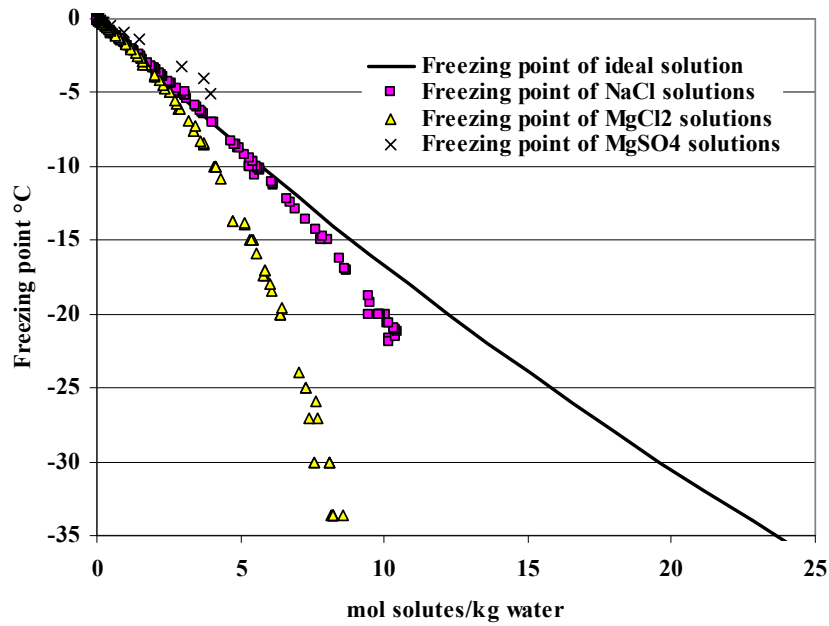


Figure 3.2: The theoretical freezing point depression of an ideal solution compared to measured freezing point depressions of sodium chloride, magnesium chloride, and magnesium sulfate solutions.

contains 2.73 moles magnesium chloride and freezes at -33.6°C . If full dissociation is assumed, this solution contains 8.19 mol of solutes (Mg^{2+} and Cl^{-} ions). This eutectic solution is therefore more dilute than the eutectic sodium chloride solution. It would be expected that the more concentrated solution would have a lower freezing point.

Magnesium sulfate solutions have higher freezing points than ideal solutions have. The same is the case for sodium sulfate solutions but the positive deviation for sodium sulfate solutions is lower than for magnesium sulfate solutions. The experimental data for sodium sulfate solutions are not shown in Figure 3.2. The eutectic solution of sodium sulfate only contains 0.84 mol solutes per kg water.

Exercise 3.2

Calculate the boiling point elevation of an ideal solution of solutes in water at 1 atm pressure. Find the appropriate Gibbs energies as a function of temperature and pressure on the internet or in steam tables. Alternatively, you can use the relation $G = H - TS$ to calculate Gibbs energies in the relevant temperature range, based on table values at 100°C and 1 atm. Compare the results with the experimental data from Hakuta *et al.* [1] given in Table 3.3. Plot the results in a graph similar to Figure 3.2.

Table 3.3: Experimental measurements of the boiling point of electrolyte solutions at 1 atm.

NaCl		Na ₂ SO ₄		MgCl ₂	
Boiling point	mass percent	Boiling point	Mass percent	Boiling point	Mass percent
100.151	0.956	100.082	1.004	100.125	0.976
100.308	1.944	100.163	2.019	100.264	2.007
100.471	2.916	100.239	2.999	100.411	3.032
100.648	3.948	100.319	4.006	100.568	4.025
100.821	4.898	100.396	5.038	100.734	5.032
100.996	5.851	100.478	6.096	100.927	6.055
101.198	6.938	100.555	7.103	101.065	6.749
101.453	8.158	100.637	8.101	101.327	7.972
101.675	9.158	100.714	9.056	101.535	8.868
101.9	10.245	100.802	10.162	101.805	9.89
102.17	11.246	100.886	11.188	102.119	10.994
102.41	12.264	100.971	12.179	102.405	11.905
102.694	13.346	101.053	13.134	102.74	12.872
102.955	14.35	101.138	14.178	103.131	13.915
103.249	15.362	101.228	15.174	103.594	15.116

1 Hakuta T., Goto T., Ishizaka S., “Boiling point elevation of Aqueous Solutions Containing Inorganic Salts”, Nippon Kaisui Gakkai-Shi, 28(1974)151-155

4 Chemical potential and activity coefficients

4.1 Chemical potential

The chemical potential μ_i of a species i is the partial molar derivative of the total Gibbs energy G , enthalpy H , Helmholtz energy A , or internal energy U of substance i [2]:

$$\mu_i \equiv \left[\frac{\partial G}{\partial n_i} \right]_{T,P,n_j} = \left[\frac{\partial H}{\partial n_i} \right]_{S,P,n_j} = \left[\frac{\partial A}{\partial n_i} \right]_{T,V,n_j} = \left[\frac{\partial U}{\partial n_i} \right]_{S,V,n_j} \quad (4.1)$$

In equation (4.1), n_i is the amount of component i , T is the temperature, P is the pressure, S is the entropy, and V is the volume.

Matter flows spontaneously from a region of high chemical potential to a region of low chemical potential just like electric current flows from a region of high electric potential to a region of low electric potential and mass flows from a position of high gravitational potential to a position of low gravitational potential. The chemical potential can therefore be used to determine whether or not a system is in equilibrium. When the system is in equilibrium, the chemical potential of each substance will be the same in all phases of the system.

The chemical potential of a species in its standard state is identical to its molar standard state Gibbs energy. Equation (3.1) can therefore be rewritten:

$$\mu_i^{id} = \mu_i^0 + RT \ln x_i \quad (4.2)$$

4.2 Excess chemical potentials for real solutions

It was shown in chapter 3 that aqueous salt solutions deviate significantly from ideal solution behavior. In order to describe phase equilibria of electrolyte solutions it is therefore necessary to introduce a correction for the deviation from ideal solution behavior. The difference between the chemical potential of a real solution and that of an ideal solution is called the excess chemical potential. The excess chemical potential for component i is $\mu_i^{ex} = RT \ln \gamma_i$. γ_i is the activity coefficient of component i . The activity coefficient is a function of composition, temperature and pressure. By including this excess term, the chemical potential of component i in a real solution is expressed as:

$$\begin{aligned} \mu_i &= \mu_i^{id} + \mu_i^{ex} \\ &= \mu_i^0 + RT \ln x_i + RT \ln \gamma_i \\ &= \mu_i^0 + RT \ln (x_i \gamma_i) \end{aligned} \quad (4.3)$$

The chemical potential of water in an aqueous solution can be calculated from the definition in equation (4.1) and expressed through an equation of the form given in equation (4.3):

$$\mu_w = \left(\frac{\partial G}{\partial n_w} \right)_{P,T,n_{i \neq w}} = \mu_w^0 + RT \ln (x_w \gamma_w) \quad (4.4)$$

As shown in chapter 3, dilute solutions are exhibiting ideal solution behavior. In the limit of $x_w \rightarrow 1$ it follows that $\gamma_w = 1$ and the excess chemical potential vanishes. The excess term is

2 Prausnitz J.M., Lichtenthaler R.N., Azevedo E.G, "Molecular Thermodynamics of Fluid-Phase Equilibria", third edition, Prentice Hall PTR, Upper Saddle River NJ 07458, 1999

only relevant for mixtures. The standard state chemical potential of water, μ_w^0 is identical to the molar Gibbs energy of pure liquid water at temperature T and pressure P .

4.3 The rational, unsymmetrical activity coefficient

The chemical potential of an ion i may be written as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_{j \neq i}} \quad (4.5)$$

The operation implied in equation (4.5) is physically impossible. Because of the electro neutrality constraint it is not possible to add ions of one type keeping the number of all other ions constant at the same time. Therefore it is not possible to measure the properties of a single ion independent of other ions. What is measured is therefore always the sum of the properties of an anion and a cation. In order to get numerical values of the standard state properties of single ions, the properties of one ion are given fixed values. By convention, the standard state chemical potential of the hydrogen ion H^+ is 0 J/mol. Similarly, by convention the enthalpy of formation, the standard state heat capacity and the standard state partial molar volume of the hydrogen ion are given the value 0. The properties measured for HCl in dilute solutions then become the properties of the chloride ion.

It is of course possible mathematically to write an expression similar to equation (4.4) for ion i :

$$\mu_i = \mu_i^0 + RT \ln(x_i \gamma_i) \quad (4.6)$$

In equation (4.6), the same standard state (pure ion i) is used as in equation (4.4). It is not possible to have “pure ion i ”. This standard state is therefore not physically possible but is a hypothetical or mathematical state used because it is convenient to use the same definition for all components.

Traditionally, the activity coefficients of solutes are normalized so that the activity coefficient of a solute is 1 at infinite dilution. This is achieved by defining a new activity coefficient γ_i^* by the ratio of the value of the activity coefficient at the relevant concentration and the value of the activity coefficient at infinite dilution, γ_i^∞ :

$$\gamma_i^* = \frac{\gamma_i}{\gamma_i^\infty} \quad (4.7)$$

The infinite dilution activity coefficient of a component in water is depending on temperature and pressure. It is clear from equation (4.7) that $\gamma_i^* = 1$ at infinite dilution. γ_i^* is the rational, unsymmetrical, activity coefficient. The adjective “unsymmetrical” refers to the fact that this activity coefficient has a value of unity at infinite dilution rather than in the pure component state. The definition in equation (4.7) is often referred to as a “normalization” of the symmetrical activity coefficient. The rational, unsymmetrical activity coefficient can be used in an expression for the chemical potential of ion i similar to equation (4.6):

$$\begin{aligned} \mu_i &= \mu_i^0 + RT \ln(x_i \gamma_i) \\ &= \mu_i^0 + RT \ln \gamma_i^\infty + RT \ln(x_i \gamma_i^*) \\ &= \mu_i^* + RT \ln(x_i \gamma_i^*) \end{aligned} \quad (4.8)$$

The rational, unsymmetrical standard state chemical potential is defined by:

$$\mu_i^* \equiv \mu_i^0 + RT \ln \gamma_i^\infty \quad (4.9)$$

This standard state chemical potential was introduced in equation (4.8) in order to get a formulation similar to the one in equation (4.6).

4.4 The molality activity coefficient

The relation between the mole fraction and the molality of a solute species was derived in equation (2.9):

$$x_i = \frac{n_i}{\sum n_j} = \frac{n_i}{\sum n_j} \frac{n_w M_w}{n_w M_w} = m_i x_w M_w \quad (2.9)$$

By using this relation, the molality concentration unit can be introduced into equation (4.8):

$$\begin{aligned} \mu_i &= \mu_i^* + RT \ln(x_i \gamma_i^*) \\ &= \mu_i^* + RT \ln(m_i x_w M_w \gamma_i^*) \\ &= \mu_i^* + RT \ln(M_w m_0) + RT \ln(m_i x_w \gamma_i^* / m_0) \end{aligned} \quad (4.10)$$

In order to make the terms dimensionless, $m_0 = 1$ mol/kg water has been introduced. A molality activity coefficient is now defined:

$$\gamma_i^m \equiv x_w \gamma_i^* \quad (4.11)$$

The molality based standard state chemical potential μ_i^m is defined:

$$\begin{aligned} \mu_i^m &\equiv \mu_i^* + RT \ln(M_w m_0) \\ &= \mu_i^0 + RT \ln(\gamma_i^\infty M_w m_0) \end{aligned} \quad (4.12)$$

By introducing the terms for the molality activity coefficient and the term for the molality based standard state in equation (4.10) it can be written:

$$\mu_i = \mu_i^m + RT \ln(\gamma_i^m m_i / m_0) \quad (4.13)$$

μ_i^m is the chemical potential of solute i in a hypothetical, ideal solution ($\gamma_i^m = 1$) at unit molality. By inserting $m_i = 1$ mol/kg water and $\gamma_i^m = 1$ in equation (4.13) the chemical potential therefore becomes identical to μ_i^m . The term $m_0 = 1$ mol/kg water is usually omitted from equation (4.13).

The molality based standard state chemical potential μ_i^m is often given in tables of standard state properties of electrolytes. One such table has been published by the US National Institute of Science and Technology [3].

The reason why the unsymmetrical activity coefficient is used for ions is that the standard state properties for this standard state can easily be measured. The corresponding values for the pure component standard state with symmetric activity coefficients on the other hand, cannot be measured for ions.

4.5 The molarity activity coefficient

The molarity concentration unit can also be used for expressing the chemical potential of a solute. In order to derive this expression, the molar volume $\hat{V}_{solution}$ is introduced. It is the volume per mol of solution. The molar volume of the solution is derived from equation (2.3):

$$\hat{V}_{solution} = \frac{V_{solution}}{\sum_j n_j} = \frac{\sum_j x_j M_j}{d_{solution}} \quad (4.14)$$

The relation between the mole fraction and the molarity of a solute species was derived in equation (2.10). By using this expression, the molarity concentration unit can be introduced into equation (4.8):

$$\begin{aligned} \mu_i &= \mu_i^* + RT \ln \left(\frac{c_i V_{solution}}{\sum_j n_j} \gamma_i^* \right) \\ &= \mu_i^* + RT \ln \left(\hat{V}_w c_i \frac{\hat{V}_{solution}}{\hat{V}_w} \gamma_i^* \right) \\ &= \mu_i^c + RT \ln \left(\frac{c_i}{c_0} \frac{\hat{V}_{solution}}{\hat{V}_w} \gamma_i^* \right) \end{aligned} \quad (4.15)$$

\hat{V}_w is the molar volume of water. In order to make the expression dimensionless, the factor $c_0 = 1$ mol/liter has been introduced. A molarity activity coefficient is defined by:

$$\begin{aligned} \gamma_i^c &\equiv \frac{\hat{V}_{solution}}{\hat{V}_w} \gamma_i^* \\ &= \frac{\hat{V}_{solution}}{\hat{V}_w} \frac{1}{x_w} \gamma_i^m \end{aligned} \quad (4.16)$$

It can be shown that the molarity activity coefficient can be calculated from the molality activity coefficient using the expression:

$$\gamma_i^c = \frac{m_i d_w}{c_i} \gamma_i^m \quad (4.17)$$

It follows from equation (4.14) and equation (4.15) that the molarity based standard state chemical potential of component i , μ_i^c , is defined by:

$$\begin{aligned} \mu_i^c &= \mu_i^* + RT \ln \left(\hat{V}_w c_0 \right) = \mu_i^* + RT \ln \left(\frac{M_w}{d_w} c_0 \right) \\ &= \mu_i^m + RT \ln \left(\frac{c_0}{m_0} \frac{1}{d_w} \right) \\ &= \mu_i^0 + RT \ln \left(\frac{\gamma_i^\infty M_w c_0}{d_w} \right) \end{aligned} \quad (4.18)$$

Calculations of the chemical potential can then be performed using the simple expression:

$$\mu_i = \mu_i^c + RT \ln(\gamma_i^c c_i / c_0) \quad (4.19)$$

Due to the temperature and pressure dependence of the molarity concentration unit, the molar activity coefficient is seldom calculated directly from models. If molarity activity coefficients are needed, activity coefficients are usually calculated on the mole fraction scale or molality scale and then converted to the molarity scale using equation (4.16) or (4.17). Molarity activity coefficients will therefore not be treated further in this book.

4.6 The activity of species

The activity of water is defined as the mole fraction of water multiplied by the activity coefficient of water:

$$a_w \equiv x_w \gamma_w \quad (4.20)$$

For solutes, a different activity is defined for each type of activity coefficient:

$$\begin{aligned} a_i &\equiv x_i \gamma_i && \text{when the symmetrical activity coefficient is used} \\ a_i^* &\equiv x_i \gamma_i^* && \text{when the rational, unsymmetrical activity coefficient is used} \\ a_i^m &\equiv m_i \gamma_i^m && \text{when the molality activity coefficient is used} \end{aligned} \quad (4.21)$$

4.7 Chemical potential of a salt

The total Gibbs energy for a solution of salts may be written as a sum of the contributions from water and ions:

$$G = n_w \mu_w + \sum_{ions} n_i \mu_i \quad (4.22)$$

The chemical potential of a salt S can be calculated according to equation (4.1):

$$\mu_S = \left(\frac{\partial G}{\partial n_S} \right)_{P,T,n} \quad (4.23)$$

The chemical potential of a salt, μ_S is a physical property of the solution and can be evaluated directly from experimental data.

Salt S dissociates into ν_C cations C and ν_A anions A according to equation (1.1). For salt S in solution, the total Gibbs energy can be expressed by:

$$G = n_w \mu_w + n_S \nu_C \mu_C + n_S \nu_A \mu_A \quad (4.24)$$

A partial molar differentiation is performed according to equation (4.23) at constant temperature, pressure, and mole number of water:

$$\mu_S = \frac{\partial G}{\partial n_S} = n_w \frac{\partial \mu_w}{\partial n_S} + \nu_C \mu_C + n_S \nu_C \frac{\partial \mu_C}{\partial n_S} + \nu_A \mu_A + n_S \nu_A \frac{\partial \mu_A}{\partial n_S} \quad (4.25)$$

The Gibbs-Duhem equation is at constant temperature and pressure expressed as:

$$\sum_i n_i d\mu_i = 0 \quad (4.26)$$

For an aqueous solution of a single salt, S , the Gibbs-Duhem equation gives:

$$n_w d\mu_w + n_S \nu_C d\mu_C + n_S \nu_A d\mu_A = 0 \quad (4.27)$$

The corresponding terms in equation (4.25) therefore cancel. By rearranging the remaining terms, they can be written as:

$$\mu_S = (\nu_C \mu_C^m + \nu_A \mu_A^m) + RT \ln \left(m_C^{\nu_C} m_A^{\nu_A} (\gamma_C^m)^{\nu_C} (\gamma_A^m)^{\nu_A} \right) \quad (4.28)$$

A mean molality and a mean molal activity coefficient are defined. Both are given the subscript \pm to indicate that this is an average (geometrical mean) of the value for the cation and the anion. The mean molality is defined as:

$$m_{\pm} \equiv \left(m_C^{\nu_C} m_A^{\nu_A} \right)^{1/\nu} \quad (4.29)$$

The mean molal activity coefficient is defined in a similar way:

$$\gamma_{\pm}^m \equiv \left((\gamma_C^m)^{\nu_C} (\gamma_A^m)^{\nu_A} \right)^{1/\nu} \quad (4.30)$$

The Greek letter ν is the sum of the stoichiometric coefficients:

$$\nu = \nu_A + \nu_C \quad (4.31)$$

If the standard state chemical potential of the salt in solution is written as:

$$\mu_S^m = \nu_C \mu_C^m + \nu_A \mu_A^m \quad (4.32)$$

Equation (4.28) can now be written as:

$$\mu_S = \mu_S^m + \nu RT \ln (m_{\pm} \gamma_{\pm}^m) \quad (4.33)$$

If instead mole fractions and rational activity coefficients were used, the expression for the chemical potential of the salt would be:

$$\mu_S = \mu_S^* + \nu RT \ln (x_{\pm} \gamma_{\pm}^*) \quad (4.34)$$

In equation (4.34), $\mu_S^* = \nu_C \mu_C^* + \nu_A \mu_A^*$. The mean mole fraction is given by:

$$x_{\pm} = \left(x_C^{\nu_C} x_A^{\nu_A} \right)^{1/\nu} \quad (4.35)$$

The mean, rational, unsymmetrical activity coefficient is given by:

$$\gamma_{\pm}^* = \left((\gamma_C^*)^{\nu_C} (\gamma_A^*)^{\nu_A} \right)^{1/\nu} \quad (4.36)$$

Equation (4.28) can be derived in a simpler way: The total Gibbs energy for a solution of salts may be written as a sum of the contributions from water and salts:

$$G = n_w \mu_w + \sum_{salts} n_s \mu_s \quad (4.37)$$

By equating (4.22) and (4.37) the following equation is obtained:

$$\sum_{salts} n_s \mu_s = \sum_{ions} n_i \mu_i \quad (4.38)$$

For salt S in solution, the chemical potential can therefore be expressed as:

$$n_s \mu_s = n_s \nu_C \mu_C + n_s \nu_A \mu_A \quad (4.39)$$

By combining with equation (4.13) for the ions C and A , equation (4.28) is obtained directly.

Exercise 4.1

Show how equation (4.17) can be derived from equation (4.16).

Exercise 4.2

Calculate the rational, unsymmetrical standard state chemical potential and the pure component standard state chemical potentials for the sodium ion and the chloride ion at 25°C.

At this temperature, the infinite dilution activity coefficient of the sodium ion is $\gamma_{Na^+}^\infty = 175.0$ and the corresponding value for the chloride ion is $\gamma_{Cl^-}^\infty = 1.549 \cdot 10^{-7}$. The molality based standard state chemical potentials of these ions can be found in Table 5.2.

Some values of the mean molal activity coefficients are given in Table 5.3. Calculate the mean rational activity coefficients and the mean symmetrical activity coefficients of sodium chloride from the mean molal activity coefficients given in that table. Plot the three types of activity coefficients in the same coordinate system. Notice that the values of the infinite dilution activity coefficients given above are not absolute values. These values were obtained by defining the infinite dilution activity coefficient of the hydrogen ion to be one at 25 °C and 1 bar.

Calculate the ideal and the excess part of the chemical potential of sodium chloride in aqueous solutions as a function of the composition. Plot the results in graphs. Make also a plot of the total chemical potential of NaCl in aqueous solutions. Use this graph to explain why an aqueous NaCl solution is saturated at a concentration slightly higher than 6 molal.

5 Measurement of chemical potentials in salt solutions

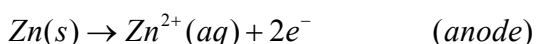
5.1 Measurement of the chemical potentials of ions

The numerical values of the Gibbs energies of formation of ions in their standard state are apparently required in order to perform phase equilibrium calculations for solutions containing electrolytes. The accurate measurement of these Gibbs energies is therefore important.

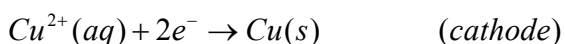
In voltaic [4] or galvanic [5] cells chemical energy can be converted to electrical energy. The reaction between metallic zinc and copper ions in a solution of copper sulfate is one such example:



The reaction can be divided into two half-reactions:



and (5.2)



In a Daniell [6] cell, these two half cell reactions are taking place in two chambers separated by a porous membrane that allow sulfate ions to pass from the cathode to the anode and thus conducting electricity. The anode and the cathode are connected with a wire allowing electrons to be transported from the anode to the cathode. The membrane that separates the two chambers gives rise to a so-called liquid junction potential. In order to avoid the liquid junction potential, the two chambers can instead be connected with a salt bridge. A salt bridge is a tube filled with a concentrated solution of a salt. The salt bridge conducts electricity between the two chambers but prevents the two solutions from being mixed. The solution in the salt bridge can be prevented from mixing with the solutions of the two chambers by adding agar.

The ability of a cell to create a difference in electrical potential is measured by its electromotive force, which is measured in volts ($1\text{V} = 1\text{ J/C}$). The electromotive force E of a voltaic cell is identical to the electrical potential at the cathode minus the electrical potential at the anode. The amount of electrical work performed by the reaction on an infinitesimal charge at constant temperature, pressure, and composition is therefore identical to the product of the charge and the electromotive force. It follows that the Gibbs energy change of the sum of the two cell reactions can be described by the following expression:

$$-v_e F E = \Delta_r G \quad (5.3)$$

The negative sign on the left hand side signifies that the charge transported consists of electrons and thus is negative. $F=96485\text{ C/mol}$ is Faradays constant and v_e is the stoichiometric coefficient of the electrons in the half-reactions. The electromotive force is depending on the temperature, pressure, and the composition of the electrolyte solutions. When the cell reaction has reached equilibrium, the electromotive force of the cell is zero.

4 Alessandro Volta (1745-1827), Italian physicist whose invention of the electric battery in the year 1800 provided the first source of continuous current

5 Luigi Galvani (1737-1798), Italian physiologist who discovered the effects of electricity on animal nerves and muscles.

6 John Daniell (1790-1845), British chemist, developed the Daniell cell in 1836

By using equation (4.13) omitting $m_0=1$ mol/kg, equation (5.3) for the cell reaction in equation (5.1) can be converted to:

$$\begin{aligned} -2FE &= \mu_{Zn^{2+}}^m + RT \ln \left(a_{Zn^{2+}}^m a_{SO_4^{2-}}^m \right) - \mu_{Cu^{2+}}^m - RT \ln \left(a_{Cu^{2+}}^m a_{SO_4^{2-}}^m \right) \\ &= \mu_{Zn^{2+}}^m - \mu_{Cu^{2+}}^m + RT \ln \left(\frac{a_{Zn^{2+}}^m a_{SO_4^{2-}}^m}{a_{Cu^{2+}}^m a_{SO_4^{2-}}^m} \right) \end{aligned} \quad (5.4)$$

The sulfate ion does not participate in the electrode reactions, but as the reactions take place in two different chambers, the concentration of sulfate ion will be different in the two chambers. Therefore the activity of the sulfate ion is included in equation (5.4).

In the limit of infinite dilution the molal activity coefficients approach 1. Provided that the exact concentrations of the two ions are known, the difference between their molal standard state chemical potentials can be calculated from electromotive force measurements performed in the vicinity of infinite dilution. For such measurements to be reliable, it is required that no electrical current is flowing. If there is an appreciable amount of electrical current, concentration and temperature will change during the experiment. By using a potentiometer, the exact electromotive force of the cell can be measured without the flow of electrons.

5.2 The Nernst equation

The general form of equation (5.4) is:

$$E = E^0 - \frac{RT}{\nu_e F} \ln \left(\frac{\text{molal activity product of products}}{\text{molal activity product of reactants}} \right)$$

with the standard potential

$$E^0 = \frac{\Delta_r G^m}{-\nu_e F} \quad (5.5)$$

"products" and "reactants" refer to the total reaction

$\Delta_r G^m$ is the change in molal standard state gibbs energy by the total reaction

Equation (5.5) was first formulated in 1889 by the German physical chemist Hermann Walther Nernst and is known as the Nernst equation.

From the derivation of the Nernst equation (5.5) it can be seen that the introduction of the unsymmetrical activity coefficient provides the necessary framework for measuring standard state chemical potentials. Obviously the rational, unsymmetrical reference system could as well be used in the Nernst equation (5.5). The use of the symmetrical reference system would not work in the Nernst equation, because it would require that measurements were carried out in a concentration range that cannot be realized physically.

When a standard hydrogen electrode is used as either anode or cathode, it is possible to measure the difference between the standard state chemical potential of the metal ion in the other half reaction and the standard state chemical potential of the hydrogen ion. The latter is by convention equal to zero. Metal ions having a positive molal standard state chemical potential can act as cathodes with the standard hydrogen electrode as anode. Metal ions with a negative molal standard state chemical potential act as anodes with the standard hydrogen electrode as cathode.

5.3 The Harned cell

A Harned cell [7] is a cell consisting of a standard hydrogen electrode and a silver chloride electrode. For a standard hydrogen electrode the half cell reaction is

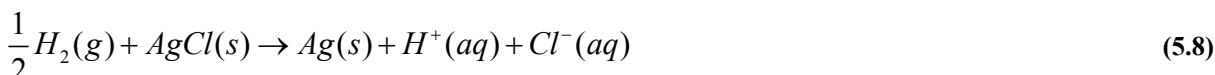


The hydrogen electrode is a standard hydrogen electrode (SHE) when the partial pressure of hydrogen in the cell is 1 bar.

If a silver chloride electrode is used as cathode, the other half cell reaction is:



The sum of the two half reactions are:



The Nernst equation for this cell is:

$$E = E^0 - \frac{RT}{F} \ln \left(\frac{m_{H^+} \gamma_{H^+}^m m_{Cl^-} \gamma_{Cl^-}^m}{P_{H_2}^{1/2}} \right) \quad (5.9)$$

The partial pressure of hydrogen is adjusted to one bar and the equation reduces to:

$$E = E^0 - \frac{RT}{F} \ln (m_{H^+} \gamma_{H^+}^m m_{Cl^-} \gamma_{Cl^-}^m) = E^0 - \frac{2RT}{F} \ln (m_{HCl} \gamma_{\pm}^m) \quad (5.10)$$

The standard potential of this cell is:

$$E^0 = \frac{\mu_{H^+}^m + \mu_{Cl^-}^m - \mu_{H_2(g)} - \mu_{AgCl(s)}^0}{-F} \quad (5.11)$$

By measuring the electromotive force of this cell at high dilution and extrapolating the value to infinite dilution, the numerical value of the standard potential of the cell can be determined. When the standard potential of the cell is known, the cell can be used for determining activity coefficients of aqueous HCl solutions.

Experimentally measured electromotive force values from Harned and Ehlers [7], are given in Table 5.1. The data are plotted in Figure 5.1. The standard potential or standard electromotive force of the cell, E^0 is calculated from Equation (5.10) as a function of the molality of HCl assuming the mean molal activity coefficient to be 1. This assumption is true at zero molality.

By extrapolation of the experimental data to zero molality the value of E^0 can be found as the intersection with the ordinate axis in Figure 5.1. Because of the curvature of the line along which the data are to be extrapolated, this extrapolation cannot be done without using an accurate activity coefficient model. The extrapolation method actually used for this type of data was introduced by Hitchcock in (1928) [8]. The value of the standard electromotive force obtained by a correct extrapolation of the data in Table 5.1 is 0.22241 Volt. This point is marked in Figure 5.1.

7 Harned H.S. and Ehlers R.W., "The Dissociation Constant Of Acetic Acid From 0 To 35° Centigrade", J. Am. Chem. Soc., 54(1932)1350-1357

8 Hitchcock D.I., "The Extrapolation of Electromotive Force Measurements to Unit Ionic Activity", J. Am. Chem. Soc. 50(1928)2076-2079

Table 5.1: Electromotive force measurements performed in HCl solutions at 25°C [7].

Molality of HCl, mol/kg	EMF measured, Volt
0.003215	0.52053
0.003564	0.51527
0.004488	0.50384
0.004776	0.50084
0.005619	0.49257
0.006239	0.48747
0.007311	0.47948
0.008636	0.47135
0.009138	0.4686
0.009436	0.46711
0.011195	0.45861
0.0135	0.44938
0.013407	0.44974
0.01473	0.44512
0.0171	0.43783
0.02305	0.42329
0.02563	0.41824
0.04749	0.38834
0.05391	0.38222
0.06268	0.37499

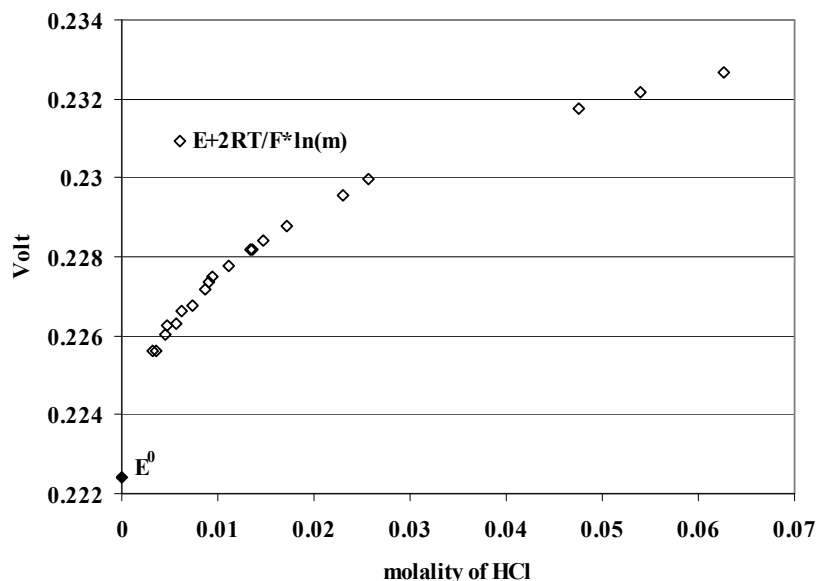


Figure 5.1: Electromotive force measurements plotted as a function of molality. By assuming ideal behavior at infinite dilution the standard electromotive force can be found by extrapolation to zero molality. An accurate extrapolation requires the use of an activity coefficient model known to be exact at infinite dilution. The value of the standard electromotive force obtained by a correct extrapolation is $E^0=0.22241$ Volt.

A variety of potentiometric cells for determination of activity coefficients and standard state chemical potentials were described by Butler and Roy [9]. These include the glass pH electrode, amalgam electrodes, cation-selective glass electrodes, liquid and polymer based ion-exchange electrodes, neutral, carrier-based electrodes, cells with transference, solid-state membrane electrodes, enzyme and other biologically based electrodes, and gas-sensitive membrane electrodes

Standard state chemical potentials for a few salts and ions are given in Table 5.2.

Exercise 5.1

Use data from Table 5.2 to determine the standard electromotive force of the Harned cell. Calculate the mean molal activity coefficients of the HCl solutions for which electromotive force measurements are available in Table 5.1.

9 Butler J.N. and Roy R.N. "Experimental Methods: Potentiometric". Chapter in "Activity coefficients in Electrolyte Solutions", 2nd Edition, Editor K.S. Pitzer, CRC Press, Boca Raton, Florida, 1991

Table 5.2: Standard state properties of ions and salts at 25°C. The values for ions are based on the molality concentration scale.

Compound	$\Delta_f G$ kJ/mol	$\Delta_f H$ kJ/mol	C_p kJ/mol/K
KCl(s)	-409.140	-436.744	0.0513
NaCl(s)	-384.138	-411.153	0.05050
K ₂ SO ₄ (s)	-1321.37	-1437.79	0.13146
AgCl(s)	-109.789	-127.068	0.05079
H ⁺ (aq)	0	0	0
K ⁺ (aq)	-283.270	-252.380	0.0218
Na ⁺ (aq)	-261.905	-240.120	0.0464
Cl ⁻ (aq)	-131.228	-167.159	-0.1364
SO ₄ ²⁻ (aq)	-744.530	-909.270	-0.293

5.4 Measurement of solvent activity

Instead of measuring the mean molal activity coefficients, chemical potentials in an electrolyte solution can be determined by measuring the activity of the solvent. By using the Gibbs-Duhem equation, experimental solvent activity coefficients can be converted to mean molal activities and vice-versa. The solvent activity in an electrolyte solution can be measured in several different ways:

5.4.1 Freezing point depression and boiling point elevation measurements

The principle for freezing point depression measurements were described in chapter 3. The activity coefficient of the solvent can be calculated from the difference between the measured freezing point depression and the freezing point depression expected from ideal solution behavior. The same applies to boiling point elevations. Equation (3.11) is valid for ideal solution behavior:

$$\Delta_f G_w^0(T, P) + RT \ln x_w = \Delta_f G_{ice}^0(T, P) \quad \text{for freezing point depression}$$

and

$$\Delta_f G_w^0(T, P) + RT \ln x_w = \Delta_f G_{steam}^0(T, P) \quad \text{for boiling point elevation}$$

By introducing the solvent activity coefficient, the equations become valid for real solutions:

$$\Delta_f G_w^0(T, P) + RT \ln(x_w \gamma_w) = \Delta_f G_{ice}^0(T, P) \quad \text{for freezing point depression}$$

and

$$\Delta_f G_w^0(T, P) + RT \ln(x_w \gamma_w) = \Delta_f G_{steam}^0(T, P) \quad \text{for boiling point elevation}$$

Assuming that the Gibbs energy of formation of water, ice and steam is known as a function of temperature and pressure, the only unknown in equation (5.12) is the water activity. From measurements of freezing point depression or measurement of boiling point elevation it is therefore possible to determine the water activity in aqueous electrolyte solutions. Especially freezing point depressions give very accurate values of the water activity. The measurement of freezing point depression is not very sensitive to pressure variations. The measurement of boiling point elevations on the other hand requires very accurate measurements of both

temperature and pressure.

5.4.2 Vapor pressure methods

Vapor pressures are usually measured by a static method, a dynamic method, or by the isopiestic method.

There are many variations of the static method for vapor pressure measurement. In some applications of this method, the difference between the vapor pressure of the solution and of the pure solvent is measured. In other applications, only the absolute vapor pressure of the solution is measured. Chilled mirror hygrometers measure the relative humidity of a sample by a static method. The relative humidity is identical to the water activity. In the bithermal equilibration method by Stokes [10], a steady state is established between a solution at one temperature and pure water at a lower temperature. When no evaporation/condensation takes place through the tube connecting the gas phase of the sample and that of pure water, the vapor pressure of the solution is identical to the vapor pressure of pure water at the measured temperature. This method requires a very accurate measurement of temperature but no measurement of pressure.

The dynamic method can also be applied in different ways. Ha and Chan [11] used an electro-dynamic balance to trap a small sample of the solution studied. The sample was kept floating in the air in a chamber with a constant stream of humid air flowing through. The air humidity could be varied by mixing a dry air stream with an air stream of known humidity. If the air stream had a vapor pressure of water exactly matching the equilibrium vapor pressure of the sample, the mass of the sample remained constant. By measuring the relative humidity of the air leaving the chamber the water activity of the sample was determined.

In equation (5.12) the condition for equilibrium between a solution and a gas phase is given. The equilibrium between pure liquid water and pure steam can be expressed by a similar equation:

$$\Delta_f G_w^0(T, P) = \Delta_f G_{steam}^0(T, P_{sat}) \quad (5.13)$$

The Gibbs energy of formation of the liquid phase is not very sensitive to the pressure and can be assumed independent of pressure within a large pressure range. P_{sat} is the pressure of water vapor in equilibrium with pure water at the temperature T . The pressure dependence of the vapor phase is known from fundamental thermodynamic relations. At higher pressures, P_{sat} should be replaced with the equilibrium water fugacity:

$$\Delta_f G_{steam}^0(T, P_{sat}) = \Delta_f G_{steam}^0(T, P_0) + RT \ln \frac{P_{sat}}{P_0} \quad (5.14)$$

By combining equation (5.13) and (5.14) it can be concluded that:

$$\Delta_f G_w^0(T, P) - \Delta_f G_{steam}^0(T, P_0) = RT \ln \frac{P_{sat}}{P_0} \quad (5.15)$$

The presence of ions causes a vapor pressure lowering. For a solution, the vapor pressure of water is therefore P_w instead of P_{sat} . Equation (5.12) at the same temperature can therefore be written:

10 Stokes, R.H., "The Measurement of Vapor Pressures of Aqueous Solutions by Bi-thermal Equilibration Through the Vapour Phase, J. Am. Chem. Soc., 69(1947)1291-1296

11 Ha, Z.; Chan, C.K. "The Water Activities of $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, and Their Mixtures", Aerosol Science and Technology 31(1999)154-169 (16)

$$\Delta_f G_w^0(T, P) + RT \ln(x_w \gamma_w) = \Delta_f G_{steam}^0(T, P_0) + RT \ln \frac{P_w}{P_0} \quad (5.16)$$

The result from equation (5.15) is inserted into equation (5.16) to give:

$$RT \ln \frac{P_{sat}}{P_0} + RT \ln(x_w \gamma_w) = RT \ln \frac{P_w}{P_0}$$

$$\Downarrow \quad (5.17)$$

$$P_{sat} x_w \gamma_w = P_w$$

After measuring the vapor pressure of water it is very simple to calculate the water activity coefficient from equation (5.17).

5.4.3 Isopiestic measurements

The isopiestic method for determining the solvent activity was introduced by Bousfield [12]. In this method the solvent activity of a sample is determined by bringing the sample in equilibrium with a reference solute of known water activity. The majority of vapor pressure measurements on electrolyte solutions are made by the isopiestic method. Isopiestic means “of equal pressure”. A known amount of the salt under study is placed in a dish. With mixtures of salts, several samples can be put in separate dishes simultaneously. In another dish a known amount of a reference solute with known water activity such as sodium chloride is placed.

Sometimes more than one reference solute is used in separate dishes. Water is added to the dishes, which are placed in a container and brought into good thermal contact at a given temperature. This is achieved by containing the samples in metal dishes of high thermal conductivity such as silver or platinum. The dishes rest on a thick copper block. Water will distill off the samples with high water activity and condense in samples with low water activity. After several days or weeks, the salt solutions in the dishes will be in equilibrium with each other through the common vapor phase. The masses of the dishes are then measured in order to determine the amount of water in each dish. The water activity of the reference salt solution is a known function of salt concentration. At equilibrium in the container, the water activities in all the dishes will be equal and hence the water activity of the solution of the salt under study will be known.



Figure 5.2: Isopiestic measurement performed in glass container

One disadvantage of the isopiestic method is that by this method water activities are determined relative to other water activities. In order to interpret data obtained by this method, it is therefore necessary to use direct vapor pressure measurements or potentiometric measurements in order to determine the water activity in the reference solutions.

The isopiestic method works best for solutions with a molality higher than 0.1 molal. Below this concentration the method gives unsatisfactory results. This can be explained by the fact

12 Bousfield W.R. “Vapour Pressure and Density of Sodium Chloride Solutions”, Trans. Faraday Soc. 13(1918)401

that the water activities of all dilute solutions are very close to unity. The driving force causing water to distill off one dish and condense in another dish is therefore very low and requires a very long equilibration time.

5.5 Osmotic coefficient

The activity of pure water is unity. In dilute solutions the activity and the activity coefficients are very little different from unity. This means that the water activities require a large number of significant digits to show variations with the salt concentration. This led N. Bjerrum to introduce the so-called osmotic coefficient in 1918 [13]. The osmotic coefficient introduced by Bjerrum was later termed the “rational” osmotic coefficient. Bjerrum gave this rational osmotic coefficient the symbol f_0 and defined it: $f_0 \equiv \ln(x_w \gamma_w) / \ln x_w$. Later, the “practical” osmotic coefficient Φ was introduced. The computation of practical osmotic coefficient involved slightly less trouble than the computation of rational osmotic coefficients as discussed by Guggenheim [14]. This factor is not important today, but the practical osmotic coefficient is still the only one used. The practical osmotic coefficient or just “the osmotic coefficient” as it is known, is defined by:

$$\Phi \equiv \frac{-\ln a_w}{M_w \nu m_s} = -\frac{n_w}{\nu n_s} \ln a_w \quad (5.18)$$

By isopiestic measurements, the osmotic coefficient of a sample is determined relative to the osmotic coefficient of a known electrolyte. It is common to use the “osmotic ratio” to present such data. The osmotic ratio R is defined as the ratio between the osmotic coefficient of the sample and that of the reference:

$$R \equiv \frac{\Phi_{\text{sample}}}{\Phi_{\text{ref}}} = \frac{(\nu m)_{\text{ref}}}{(\nu m)_{\text{sample}}} \quad (5.19)$$

The osmotic coefficient of the sample solution is then related to the osmotic coefficient of the isopiestic reference solution with the equation:

$$\Phi_{\text{sample}} = R \cdot \Phi_{\text{reference}} \quad (5.20)$$

Solutions of two different salts with identical water activity have different osmotic coefficients if the stoichiometric coefficients are different. As mentioned before, absolute values for osmotic coefficients can be measured by direct measurement of the partial pressures of water over salt solutions.

It is common to use a value of $\nu = 3$ when reporting osmotic coefficients for a salt like Na_2SO_4 . For electrolytes like H_2SO_4 and NaHSO_4 , $\nu = 2$ is often used, sometimes $\nu = 3$ is used. It is important to know which stoichiometric coefficients were used for a specific set of osmotic coefficient data, in order to convert them to the correct water activity.

Table 5.3 shows some values of a_w , Φ and γ_{\pm}^m for aqueous solutions of NaCl at 25°C and 1 bar for different molalities. The water activities and the osmotic coefficients from the table are illustrated in Figure 5.3. The data shows that the water activity is almost linearly dependent of molality. The osmotic coefficient on the other hand is much more sensitive to concentration changes and has a concentration dependence that is far from linear. It is seen

13 N. Bjerrum: Die Dissoziation der starken Elektrolyte, Zeitschrift für Elektrochemie, 24(1918)321-328

14 Guggenheim E.A. “The Specific Thermodynamic Properties of Aqueous solutions of strong electrolytes”, Phil. Mag. 19(1935)588

from Figure 5.3 that a large osmotic coefficient means a low water activity.

Table 5.3: Water activities, osmotic coefficients, and mean molal activity coefficients of aqueous NaCl solutions at 25°C, a_w : water activity, Φ : osmotic coefficient, γ_{\pm}^m : mean molal activity coefficient of NaCl

m_{NaCl} mol/kg	a_w	Φ	γ_{\pm}^m
0	1.	1.	1.
0.0064	0.9997755	0.9737	0.9198
0.1	0.996646	0.9324	0.778
0.2	0.993360	0.9245	0.735
0.3	0.99009	0.9215	0.710
0.5	0.98355	0.9209	0.681
1.0	0.96686	0.9355	0.657
2.0	0.9316	0.9833	0.668
3.0	0.8932	1.0453	0.714
5.0	0.8068	1.1916	0.874
6.0	0.7598	1.2706	0.986

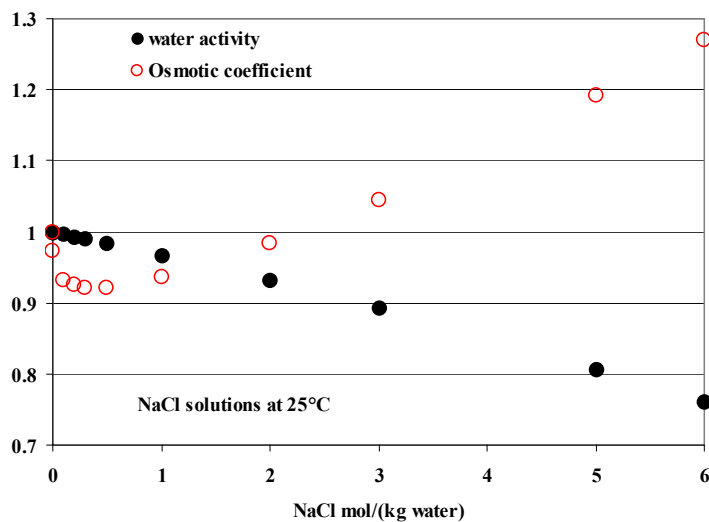


Figure 5.3: The non-ideality of water in sodium chloride solutions at 25°C, presented as water activity and as osmotic coefficients. The data are identical with the data in Table 5.3.

5.5.1 The value of the osmotic coefficient at infinite dilution

From the defining equation (5.18) the value of the osmotic coefficient at infinite dilution is not obvious.

The mole fraction of water can be written as:

$$x_w = 1 - \sum_{\text{ions}} x_i \quad (5.21)$$

By inserting the relation between mole fraction and molality, equation (2.9) the mole fraction of water can be written:

$$x_w = 1 - \sum_{\text{ions}} m_i x_w M_w \Rightarrow x_w = \frac{1}{1 + M_w \sum_{\text{ions}} m_i} = \frac{1}{1 + M_w \nu m_S} \quad (5.22)$$

The activity of water $a_w = x_w \gamma_w$. In the limit of infinite dilution the activity coefficient of water is 1. $\ln a_w$ can therefore be approximated as

$$\ln a_w = \ln(x_w \gamma_w) \approx -\ln(1 + M_w \nu m_s) \approx -M_w \nu m_s \quad (5.23)$$

By inserting this expression in the defining equation (5.18) the limiting value of Φ at infinite dilution can be determined:

$$\lim_{m_s \rightarrow 0} \Phi = -\frac{-M_w \nu m_s}{M_w \nu m_s} = 1 \quad (5.24)$$

5.6 Mean activity coefficient from osmotic coefficient

Based on the Gibbs-Duhem equation, it is possible to calculate water activities (osmotic coefficients) from electromotive force measurements (molal activity coefficients of ions). The relationship between osmotic coefficients and mean molal activity coefficients is based on the Gibbs-Duhem equation at constant temperature and pressure:

$$\sum_i n_i d\mu_i = 0 \quad (5.25)$$

For an aqueous solution of a single salt, S , this can be expressed as:

$$n_w d\mu_w + n_s d\mu_s = 0 \quad (5.26)$$

Insertion of equations (4.4) and (4.33) gives:

$$n_w d[\mu_w^0 + RT \ln(x_w \gamma_w)] + n_s d[\mu_s^m + \nu RT \ln(m_{\pm} \gamma_{\pm}^m)] = 0 \quad (5.27)$$

As the standard state chemical potentials are constant at constant temperature and pressure, this reduces to:

$$n_w d \ln a_w + n_s \nu d \ln(m_{\pm} \gamma_{\pm}^m) = 0 \quad (5.28)$$

Using the definition of the molality of a salt, equation (2.4), this is transformed into:

$$d \ln a_w + m_s M_w \nu d \ln(m_{\pm} \gamma_{\pm}^m) = 0 \quad (5.29)$$

Replacing $\ln a_w$ with the corresponding term from the definition of the osmotic coefficient in equation (5.18) gives:

$$-d[\Phi M_w \nu m_s] + m_s M_w \nu d \ln(m_{\pm} \gamma_{\pm}^m) = 0 \quad (5.30)$$

From equations (2.5), (2.6), and (4.29) it is found that $m_{\pm} = m_s (\nu_C^{\nu_C} \nu_A^{\nu_A})^{1/\nu}$. This can be used to reduce equation (5.30) further because the factor after m_s is a constant:

$$d[\Phi m_s] = m_s d \ln(m_{\pm} \gamma_{\pm}^m) \quad (5.31)$$

The differentials on both sides are expanded:

$$\Phi dm_s + m_s d\Phi = m_s d \ln m_s + m_s d \ln \gamma_{\pm}^m \quad (5.32)$$

The terms are rearranged to:

$$d \ln \gamma_{\pm}^m = d\Phi + (\Phi - 1) d \ln m_s \quad (5.33)$$

If this equation is integrated from $m_s = 0$ where $\Phi = 1$ and $\ln \gamma_{\pm}^m = 0$, the following equation is obtained:

$$\ln \gamma_{\pm}^m = \Phi - 1 + \int_0^{m_s} (\Phi - 1) \frac{dm_s}{m_s} \quad (5.34)$$

If the osmotic coefficient has been determined with small concentration intervals, equation (5.34) can be integrated graphically to give the corresponding mean molal activity coefficients. Alternatively, if the experimental data for the osmotic coefficients can be given an analytical form in the range from infinite dilution to finite molalities, the integral in equation (5.34) can be evaluated analytically.

It is also possible to go the opposite way and calculate Φ from γ_{\pm}^m . From equation (5.29) we get

$$d \ln a_w + M_w \nu dm_s + m_s M_w \nu d \ln \gamma_{\pm}^m = 0 \quad (5.35)$$

Integration from $m_s = 0$ gives

$$\ln a_w + M_w \nu m_s + M_w \nu \int_{m_s=0}^{m_s=m_s} m_s d \ln \gamma_{\pm}^m = 0 \quad (5.36)$$

Division with $M_w \nu m_s$ and using the definition of the osmotic coefficient in equation (5.18) gives:

$$\Phi = 1 + \frac{1}{m_s} \int_0^{m_s} m_s d \ln \gamma_{\pm}^m \quad (5.37)$$

If mean molal activity coefficients have been determined by a potentiometric method (measurement of electromotive force), the corresponding osmotic coefficients can be obtained by integration of equation (5.37).

The integrations proposed in equations (5.34) and (5.37) can be done graphically, but that will usually result in some inaccuracy. Osmotic coefficients measured with the isopiestic method usually do not extend to concentrations below 0.1 molal. By correlating the experimental data with a thermodynamic model that is accurate in the dilute region, the integration can be performed analytically instead of graphically. Normally the model of Debye and Hückel (see chapter 6) is used for this purpose.

5.7 Osmotic Pressure

If a container with pure water is separated from a container with a solution of salt by a semi permeable membrane that allows water but not ions to pass, water will pass from the container with pure water (with relatively high water activity) to the solution container (with relatively low water activity). Because water is attracted to the solution container, the amount of solution will increase and the pressure in the solution container will increase until equilibrium is reached. If the temperature and pressure in the pure water container is T and P_0 the chemical potential of pure water is:

$$\mu_w = \mu_w^0(T, P_0) \quad (5.38)$$

In the solution container, the temperature and pressure at equilibrium is T and P_s , and the water activity is a_w . The chemical potential of water in the solution container is therefore:

$$\mu_w = \mu_w^0(T, P_s) + RT \ln a_w \quad (5.39)$$

At equilibrium between the two containers, the chemical potential of water is the same in the two containers:

$$\mu_w^0(T, P_0) = \mu_w^0(T, P_S) + RT \ln a_w \quad (5.40)$$

The pressure dependence of the chemical potential of species i is given by:

$$\left[\frac{\partial \mu_i}{\partial P} \right]_T = V_i \quad (5.41)$$

V_i is the partial molar volume of component i . The chemical potential of a species at a certain pressure can therefore be calculated by integration of equation (5.41) assuming that the partial molar volume of the species is independent of pressure:

$$\mu_w^0(T, P_S) - \mu_w^0(T, P_0) = \int_{P_0}^{P_S} V_w dP = V_w (P_S - P_0) = V_w \Pi \quad (5.42)$$

In equation (5.42) the symbol Π is used for the pressure difference between the containers. Π is called the osmotic pressure. By introducing this result into equation (5.40) this equation can be modified to:

$$\Pi = -\frac{RT}{V_w} \ln a_w \quad (5.43)$$

The osmotic pressure is important for a biological cell to maintain its structure. Two solutions with the same osmotic pressures are said to be *isotonic*. A *hypotonic* solution is more dilute and has lower osmotic pressure. A *hypertonic* solution is more concentrated and has a higher osmotic pressure. If a biological cell is in a hypotonic environment water will flow into it and cause it to expand. If a biological cell is in a hypertonic environment, it will lose water and shrink, it becomes dehydrated.

From the definition of the osmotic coefficient in equation (5.18) it can be seen that the osmotic pressure and the osmotic coefficient are proportional to each other:

$$\Pi = \frac{RT}{V_w} \frac{v n_S}{n_w} \Phi \quad (5.44)$$

When pure water is produced from sea water, a pressure corresponding to the osmotic pressure has to be applied. This process is called reverse osmosis.

Exercise 5.2

Calculate the osmotic pressure of sodium chloride solutions at 25°C from the data given in Table 5.3. The density of sodium chloride solutions can be calculated from the equation $d = 44.5 m_{NaCl} + 997 \text{ kg/m}^3$. Assume that the partial molar volume of water is identical to the molar volume of the solution.

Textbooks on physical chemistry often give the equation for osmotic pressure of dilute solutions as $\Pi = cRT$, the van't Hoff equation [15]. In this equation, the concentration of solutes is $c \text{ mol/m}^3$. Calculate the same osmotic pressures from the van't Hoff equation and show how this equation is related to equation (5.44).

15 J.H. van 't Hoff, The Role Of Osmotic Pressure In The Analogy Between Solutions And Gases, Zeitschrift für physikalische Chemie, 1(1887)481-508

6 Thermodynamic models for electrolyte solutions

Thermodynamic models for electrolyte solutions are developed in order to be able to mathematically describe the properties and the phase behavior of solutions. For the chemical industry it is very valuable to be able to optimize processes for the production of chemicals. Electrolyte solutions are involved in many processes and it is therefore important to have good models for the description of electrolyte properties.

In order to properly model electrolyte systems, all different types of interactions: ion-ion, ion-dipole, dipole-dipole, molecule-molecule should be taken into account. The potential energy caused by ion-ion interactions is proportional to the inverse separation distance, $1/r$. Electrostatic ion-ion interactions therefore have an effect over a relatively long distance and are called long range interactions. The potential energy caused by molecule-molecule interactions is proportional to the sixth power of the inverse separation distance, $1/r^6$. These interactions are therefore called short-range interactions. The potential energy of ion-dipole interactions is proportional to $1/r^2$ and the potential energy of dipole-dipole interactions is proportional to $1/r^3$. These interactions could be called intermediate range interactions.

Most models are structured with terms representing only long range and intermediate/short range interactions.

6.1 Electrostatic interactions

6.1.1 Debye-Hückel theory

The first really successful model for the electrostatic interactions between ions in aqueous electrolyte systems was developed in 1923 by P. Debye and E. Hückel [16].

Debye and Hückel described the thermodynamics of ideal solutions of charged ions. As mentioned above, the electrostatic interactions between charged ions only represent the long range interactions in such solutions and not the short range interactions. The interactions between ions and water are not described by the Debye-Hückel model, which has led people to describe this model as a “dielectric continuum model”. In this model, the solvent only plays a role due to its relative permittivity (dielectric constant) and its density. The Debye-Hückel model can therefore not stand alone as a model for electrolyte solutions. It only represents some of the electrostatic interactions and should be combined with a term for short and intermediate range interactions in order to fully describe the properties of concentrated electrolyte solutions.

In the Debye-Hückel theory, the electrostatic force that a positive ion exerts on a negative through the solvent medium is expressed through Coulombs law:

$$F = -\frac{1}{4\pi\epsilon_0\epsilon_r} \frac{e^2}{r^2} \quad (6.1)$$

e is the electronic charge = $1.60206 \cdot 10^{-19}$ C

ϵ_0 is the permittivity in vacuum = $8.8542 \cdot 10^{-12}$ C² J⁻¹ m⁻¹

ϵ_r is the dielectric constant (relative permittivity) of the solvent (unitless). The value of the relative permittivity of water is 78.4 at 298.15K

16 Debye P., Hückel E., Zur Theorie der Elektrolyte. I. “Gefrierpunktserniedrigung und verwandte Erscheinungen”, Physikalische Zeitschrift 24(1923)185-206

r is the distance between the ions (meter).

Poisson's equation gives a relationship between the charge density ($\rho_i \text{ Cm}^{-3}$) around ion i and the electrical potential ($\psi_i \text{ J/C}$) for a sphere with radius r around ion i :

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi_i}{dr} \right) = - \frac{\rho_i}{\epsilon_0 \epsilon_r} \quad (6.2)$$

Due to the charges, the ions are not distributed evenly or randomly in the solution. Near a cation, anions tend to be in excess, near an anion, cations tend to be in excess. An ion j has an electrical potential energy of $z_j e \psi_i$ if it is in the distance r from the ion i . Debye and Hückel assumed the distribution of the ions in the solution to be a Boltzmann distribution. This assumption gives another relation between the charge density and the electrical potential:

$$\rho_i = e N_A \sum_{\text{all ions}} \frac{n_j z_j}{nV} e^{-\frac{z_j e \psi_i}{kT}} \quad (6.3)$$

n_j is the mol number of component j , z_j is the charge of component j , N_A is Avogadro's number = $6.023 \cdot 10^{23} \text{ mol}^{-1}$, k is the Boltzmanns constant = $1.381 \cdot 10^{-23} \text{ JK}^{-1}$, and T is the temperature in Kelvin, V is the molar volume of the solution.

Debye and Hückel combined the Poisson equation and the Boltzmann equation thereby eliminating the charge density. The resulting Poisson-Boltzmann equation was solved for the electrical potential ψ_i .

In their paper, Debye and Hückel finally arrived at an excess Helmholtz function for an ideal solution of charged ions. It sounds like a contradiction to have an excess Helmholtz function for an ideal solution of charged ions. Ideal solutions do not have excess terms. But as mentioned before, this excess Helmholtz function only takes the non-ideality caused by the electrostatic interactions into account and does not deal with the traditional non-ideality, caused by short range forces. The molar excess Helmholtz function for the electrostatic interactions can be expressed by the equation:

$$\frac{A^E}{RT} = -\frac{1}{3} \sum x_i z_i^2 s \kappa \chi(\kappa a_i) \quad (6.4)$$

The term s is defined by:

$$s = \frac{e^2}{4\pi\epsilon_0\epsilon_r kT} \quad (6.5)$$

The distance of closest approach to the ion i was given the symbol a_i , (a for "annäherungsabstand"). The distance of closest approach is a parameter for the radius of ion i , not its diameter. It is expected that a_i is larger than the radius of the ion, because the ions are thought to be surrounded by water that gives the ions a larger radius than the bare ion. The product κa_i is dimensionless and κ is therefore a reciprocal length. $1/\kappa$ is a characteristic length called the screening length. The screening length provides a good first estimate of the distance beyond which Coulomb interactions can be essentially ignored, as well as the size of the region near a point charge where opposite-charge counter-ions can be found. The expression for κ is:

$$\kappa = \left(\frac{e^2 N_A}{\epsilon_0 \epsilon_r kT} \frac{\sum n_i z_i^2}{nV} \right)^{1/2} \quad (6.6)$$

The function χ is given by:

$$\chi(x) = \frac{3}{x^3} \left(\frac{3}{2} + \ln(1+x) - 2(1+x) + \frac{1}{2}(1+x)^2 \right) \quad (6.7)$$

Apparently, the Helmholtz function of Debye and Hückel (6.4) has not been used by those who have developed models for electrolyte solutions. Actually this equation is usually not even mentioned. Instead, a number of simplifications of the Debye-Hückel equation have been used for model development and are often mentioned in text books.

6.1.2 Debye-Hückel Extended law

The so-called extended Debye-Hückel law represents a simplification of the original Debye-Hückel equation. The relation between Gibbs energy and Helmholtz energy is $G = A + PV$. No PV term was added to the Helmholtz function. The PV term was considered insignificant and was therefore discarded. Chemical potentials were derived from the energy function by molar differentiation at constant temperature and pressure, rather than molar differentiation at constant temperature and volume. Equation (4.1) shows how the chemical potential is derived from the different energy functions.

$$\mu_i \equiv \left[\frac{\partial G}{\partial n_i} \right]_{T,P,n_j} = \left[\frac{\partial H}{\partial n_i} \right]_{S,P,n_j} = \left[\frac{\partial A}{\partial n_i} \right]_{T,V,n_j} = \left[\frac{\partial U}{\partial n_i} \right]_{S,V,n_j} \quad (4.1)$$

A Gibbs energy function was created from the Helmholtz function in equation (6.4) by replacing the molarity concentration unit with molality and simplifying the expression for κ in equation (6.6). The density of an electrolyte solution with the molar volume V and the total volume nV can be written as:

$$d_{\text{solution}} = \frac{n_w M_w + \sum_{\text{ions}} n_i M_i}{nV} \quad (6.8)$$

This expression is converted to an expression for nV , which is inserted into equation (6.6):

$$\kappa = \left(\frac{e^2 N_A d_{\text{solution}}}{\epsilon_0 \epsilon_r kT} \frac{\sum n_i z_i^2}{n_w M_w + \sum_{\text{ions}} n_i M_i} \right)^{1/2} \quad (6.9)$$

Next, the approximation is made that the volume and the mass of the ions is zero. This approximation represents a small error for dilute solutions and a more serious error for concentrated solutions. By making this approximation, the density of the solution becomes equal to the density of pure water, $d_0 \text{ kg/m}^3$. To make the expressions simpler, the ionic strength, a concept first introduced by Lewis and Randall in 1921 [17] is introduced:

$$I = 0.5 \sum_i m_i Z_i^2 \quad (6.10)$$

The expression for κ can now be written:

17 Gilbert N. Lewis and Merle Randall, "The activity coefficient of strong electrolytes", J. Am. Chem. Soc. 43(1921)1112-1154

$$\kappa \approx \left(\frac{e^2 N_A d_0}{\varepsilon_0 \varepsilon_r kT} \frac{\sum n_i z_i^2}{n_w M_w} \right)^{1/2} = \left(\frac{2e^2 N_A d_0}{\varepsilon_0 \varepsilon_r kT} \frac{1}{2} \sum m_i z_i^2 \right)^{1/2} = \left(\frac{2e^2 N_A d_0}{\varepsilon_0 \varepsilon_r kT} \right)^{1/2} I^{1/2} \quad (6.11)$$

With this approximation, the product $s\kappa$ from equation (6.4) can be written as:

$$s\kappa \approx \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT} \left(\frac{2e^2 N_A d_0}{\varepsilon_0 \varepsilon_r kT} \right)^{1/2} I^{1/2} = 2(2\pi N_A d_0)^{1/2} \left(\frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT} \right)^{3/2} I^{1/2} \quad (6.12)$$

This approximated value of $s\kappa$ is expressed as $2AI^{1/2}$ where A is the Debye-Hückel parameter:

$$A = (2\pi N_A d_0)^{1/2} \left(\frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT} \right)^{3/2} \quad (6.13)$$

The value of the Debye-Hückel parameter A is $1.1717 \text{ (kg/mol)}^{1/2}$ at 25°C .

The term κa_i from equation (6.4) was replaced by $BaI^{1/2}$ where a is a common ion size parameter replacing the individual distance of closest approach, a_i . The ion size parameter a is often in the range $3.5\text{--}6.2 \cdot 10^{-10} \text{ m}$. B is derived from the approximated value of κ in equation (6.11)

$$B = \left(\frac{2e^2 N_A d_0}{\varepsilon_0 \varepsilon_r kT} \right)^{1/2} \quad (6.14)$$

The molar Gibbs excess function arrived at by the simplification is:

$$\begin{aligned} \frac{G_{\text{Extended Debye-Hückel}}^E}{RT} &= -x_w M_w \frac{4}{3} AI^{3/2} \chi(BaI^{1/2}) \\ &= -x_w M_w \frac{4A}{(Ba)^3} \left[\ln(1 + BaI^{1/2}) - BaI^{1/2} + \frac{(Ba)^2 I}{2} \right] \end{aligned} \quad (6.15)$$

x_w is the mole fraction of water, $M_w \text{ kg mol}^{-1}$ is the molar mass of water. The function $\chi(x)$ is given in equation (6.7).

The extended Debye-Hückel law usually gives good results for activity coefficients up to an ionic strength of about 0.1 molal. Above this concentration, short range interactions apparently give a significant contribution to the deviation from ideality. The activity coefficients are derived from the total Gibbs excess function by molar differentiation:

$$\left[\frac{\partial (nG_{\text{Extended Debye-Hückel}}^E / RT)}{\partial n_i} \right]_{T,P,n_j,j \neq i} = \ln \gamma_i^* = -Z_i^2 \frac{A\sqrt{I}}{1 + Ba\sqrt{I}} \quad (6.16)$$

The activity coefficients calculated with the extended Debye-Hückel equation are the rational activity coefficients and not the molal activity coefficients as sometimes claimed in text books.

According to the definition of the molal activity coefficient in equation (4.11), the molal activity coefficient according to the extended Debye-Hückel can be calculated from:

$$\ln \gamma_i^m = \ln(x_w \gamma_i^*) = \ln x_w - Z_i^2 \frac{A\sqrt{I}}{1 + Ba\sqrt{I}} \quad (6.17)$$

The extended Debye-Hückel mean molal activity coefficient of a salt with cation C and anion

A calculated according to the definition of the mean molal activity coefficient in equation (4.30) is:

$$\begin{aligned}\ln \gamma_{\pm}^m &= \ln x_w - \frac{1}{\nu} \sum_i \nu_i Z_i^2 \frac{A\sqrt{I}}{1 + Ba\sqrt{I}} \\ &= \ln x_w - |Z_C Z_A| \frac{A\sqrt{I}}{1 + Ba\sqrt{I}}\end{aligned}\quad (6.18)$$

The last expression in equation (6.18) is obtained from the first by using the fact that $\nu_A Z_A + \nu_C Z_C = 0$.

The activity coefficient of water calculated with the extended Debye-Hückel equation is given by:

$$\begin{aligned}\left[\frac{\partial (n G_{\text{Extended Debye-Hückel}}^E / RT)}{\partial n_w} \right]_{T,P,n_i} &= \ln \gamma_w = \frac{2}{3} M_w A I^{3/2} \sigma(Ba I^{1/2}) \\ \sigma(x) &= \frac{3}{x^3} \left\{ 1 + x - \frac{1}{1+x} - 2 \ln(1+x) \right\}\end{aligned}\quad (6.19)$$

6.1.3 Debye-Hückel limiting law

The so-called Debye-Hückel limiting law is a further simplification of the original Debye-Hückel theory.

The molar excess Gibbs energy function defining the Debye-Hückel limiting law is given by the expression:

$$\frac{G_{\text{Debye-Hückel limiting law}}^E}{RT} = -x_w M_w \frac{4}{3} A I^{3/2} \quad (6.20)$$

Compared to the excess Gibbs energy of the Extended Debye-Hückel law in equation (6.15), this corresponds to considering the value of the function $\chi(Ba I^{1/2})$ to be one.

Typical values of Ba is $1 - 1.5 \text{ (kg/mol)}^{1/2}$. Values of the function $\chi(1.5 I^{1/2})$ are shown in Figure 6.1 versus ionic strength. This function is obviously very sensitive to changes in the ionic strength. The function has a limiting value of 1 at infinite dilution. In a 1 molal solution of a 1-1 salt, the value of $\chi(1.5 I^{1/2})$ is 0.48! The “Debye-Hückel limiting law” is therefore only correct in the limit of infinite dilution.

The activity coefficients for the Debye-Hückel limiting law are derived by molar differentiation of the excess Gibbs energy function in equation (6.20):

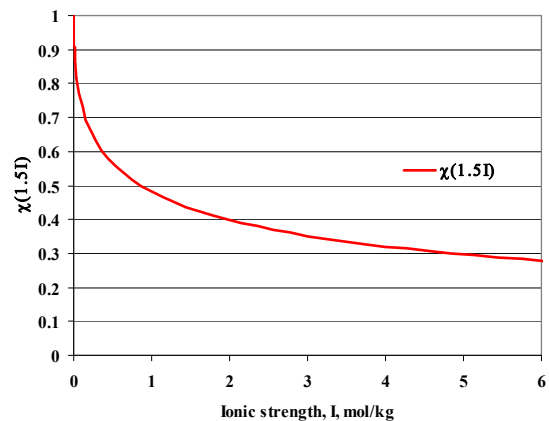


Figure 6.1: The function χ from equation (6.7) versus ionic strength

$$\left[\frac{\partial (nG_{\text{Debye-Hückel limiting law}}^E / RT)}{\partial n_i} \right]_{T,P,n_j, j \neq i} = \ln \gamma_i^* = -Z_i^2 A \sqrt{I} \quad (6.21)$$

Equation (6.21) is only applicable up to an ionic strength of maximum 0.001 molal, i.e. only for extremely dilute solutions. The corresponding mean molal activity coefficient is:

$$\ln \gamma_{\pm}^m = \ln x_w - |Z_C Z_A| A \sqrt{I} \quad (6.22)$$

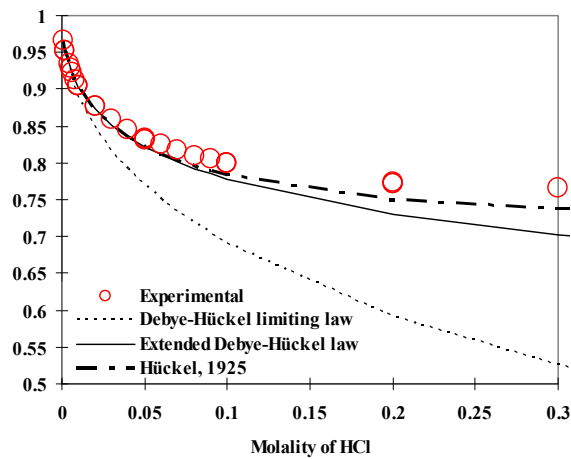


Figure 6.2: The rational mean ionic activity coefficient of aqueous HCl at concentrations up to 0.3 molal, experimental and calculated values.

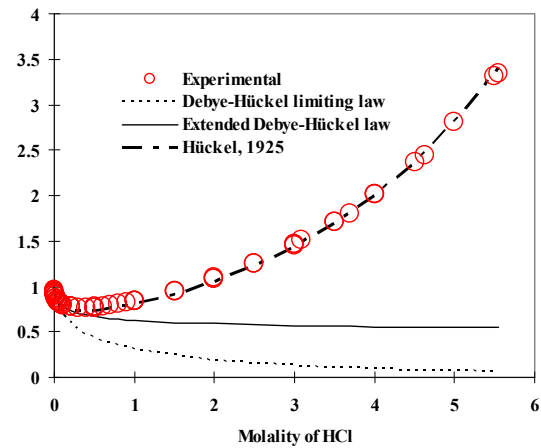


Figure 6.3: The rational mean ionic activity coefficient of aqueous HCl at concentrations up to 6 molal, experimental and calculated values.

Exercise 6.1

Show that the water activity coefficient according to the Debye-Hückel limiting law is:

$\ln \gamma_w = \frac{2}{3} M_w A I^{3/2}$. Hint: Use the Gibbs-Duhem equation (see section 5.6) and use the molality of salt as integration variable. Alternatively the activity coefficient can be derived from the excess Gibbs energy function for the Debye-Hückel limiting law.

Calculate the osmotic coefficient of water in sodium chloride solutions using water activities from the Debye-Hückel limiting law and compare the results with the experimental values of these osmotic coefficients given in Table 5.3. Use $A = 1.17165 \text{ (kg/mol)}^{1/2}$ and $B_a = 1.5 \text{ (kg/mol)}^{1/2}$.

6.1.4 The Hückel equation

In 1925 it was found by E. Hückel [18] that the addition of an extra parameter, C to the extended Debye-Hückel law made it possible to calculate activity coefficients up to higher concentrations with good accuracy. With the C parameter, a term proportional to the ionic strength was added to the logarithm of the rational, unsymmetrical activity coefficient:

18 Hückel E. "Zur Theorie konzentrierter wässriger Lösungen starker Elektrolyte", Physikalische Zeitschrift 26(1925)93-147

$$\ln \gamma_{\pm}^* = -|Z_C Z_A| \frac{A\sqrt{I}}{I + Ba\sqrt{I}} + CI \quad (6.23)$$

In his paper, E. Hückel justified the addition of the C parameter by showing that according to theory, a term proportional to the ionic strength would take the variation of the dielectric constant with the composition into account.

The performances of the Debye-Hückel limiting law, the Debye-Hückel extended law, and the Hückel equation are illustrated in Figure 6.2 and Figure 6.3. In these figures, the calculated activity coefficients of aqueous hydrochloric acid solutions are plotted together with experimental values from a number of sources. For the preparation of Figure 6.2 and Figure 6.3, a value of $1.5 \text{ (kg/mol)}^{1/2}$ was used for Ba in equations (6.16) and (6.23). The best value of the C parameter in equation (6.23) was determined to be $C = 0.321 \text{ kg/mol}$.

Figure 6.3 shows that the C parameter in the Hückel equation expands the concentration range in which the Debye-Hückel theory can be applied considerably. The C parameter is a function of temperature and of the ions in the solution.

In dilute solutions the activity coefficients of electrolytes decrease with increasing concentration, see Figure 6.2. For very dilute solutions the slope of the activity coefficient curve versus concentration will be minus infinity. For most electrolytes the activity coefficients will pass through a minimum and increase again at high concentrations reaching values which may be much higher than unity. Some systems however, show a behavior where the activity coefficient continues to drop for increasing concentration.

Exercise 6.2

Show by using the Gibbs-Duhem equation (4.26), that the effect of the C parameter in the Hückel equation (6.23) on the natural logarithm of the water activity coefficient is a contribution of $-\frac{M_w C}{|Z_C Z_A|} I^2$ to $\ln \gamma_w$.

Determine the C parameter for NaCl at 25°C based on the experimental values of the mean molal activity coefficients in Table 5.3. Use the Hückel equation with $Ba=1.5 \text{ (kg/mol)}^{1/2}$ and $A=1.17165 \text{ (kg/mol)}^{1/2}$ to perform the calculations. Use the C parameter to calculate osmotic coefficients for sodium chloride solutions. Compare these calculated osmotic coefficients with values calculated with the extended Debye-Hückel law and with experimental values given in Table 5.3.

Exercise 6.3

The generally accepted correct method for extrapolating electromotive force measurements [8] to infinite dilution requires the use of the Hückel equation. Use the Hückel equation with $Ba=1.5 \text{ (kg/mol)}^{1/2}$ and $A=1.17165 \text{ (kg/mol)}^{1/2}$ to calculate the standard electromotive force of the Harned cell based on the experimental measurements in Table 5.1. Note that a value of the Hückel C parameter needs to be determined at the same time. Hint: combine the Hückel equation with the Nernst equation to get an equation of the form: $y = E^0 - \frac{2RT}{F} CI$.

Determine E^0 and C from the data for this equation. Plot the data.

6.1.5 The Born equation

While the Debye-Hückel theory deals with the interaction between charged ions, Born [19] derived an equation for the interaction between an ion and the surrounding solvent. Around an electrical charge there is an electrostatic field. Polar molecules are affected by such fields and redirect themselves to have as low energy as possible in the field. The positive part of a polar molecule is attracted to a negative charge and vice versa for the negative part. A orientation polarization is taking place.

A solvent consisting of polar molecules is polarizable and is also referred to as a dielectric medium. Highly polarizable solvents have high relative permittivities (dielectric constants). As expressed by Coulomb's law in equation (6.1), electrostatic interactions are lowered by solvents with a high relative permittivity. Salts do not dissociate spontaneously in a vacuum because the electrostatic interactions between the ions are too strong. In water, the electrostatic interactions between ions are lowered by a factor $\epsilon_r = 78.4$ at 25 °C. The water molecules are shielding the ions from each other and allowing them to be separate.

The relative permittivity of a solvent is defined as the ratio between the permittivity of the solvent and the permittivity of vacuum:

$$\epsilon_r \equiv \frac{\epsilon}{\epsilon_0} \quad (6.24)$$

Previously, the relative permittivity was called the dielectric constant and it was referred to as D . The relative permittivity of a medium can be measured by exposing the medium to a perturbing external electromagnetic field of small field strength. The medium is placed between the plates (conductors) of a capacitor. The response of the medium to this field is measured, and from this response, the relative permittivity of the medium can be deduced. Further information on the measurement of relative permittivity can be found in the book by Hill *et al.* [20] and in the paper by Kaatzé [21].

When ions are dissolved in a dielectric medium, the solvent molecules are polarized by the electrical charges. This ion-solvent interaction is called solvation. For the special case of water as solvent, the term hydration is used instead. Here, hydration is not the formation of ion-hydrates of a specific stoichiometric composition, but the redirection of the polar water molecules around the charged ions. The energy change associated with solvation is the solvation energy or in the special case of water, the hydration energy.

Consider a spherical ion with charge Z_i and radius r_i in a medium with the permittivity $\epsilon_0 \epsilon_r$. Born calculated the solvation energy of this ion by integrating the energy of the electrical field from the surface of the spherical ion to infinity. Born found the electrostatic contribution to the Helmholtz energy of the ion to be:

$$A = -\frac{Z_i^2 e^2}{8\pi\epsilon_0 \epsilon_r r_i} \quad (6.25)$$

The expression was derived for a single ion in a solvent with the relative permittivity ϵ_r . When more ions are present, the electrostatic fields generated by the ions influence each

19 Born M., "Volumen und Hydratationswärme der Ionen", Zeitschrift für Physik, 1(1920)45-49

20 Hill N.E., W.E. Vaughan, A.H. Price, and M. Davies, "Dielectric Properties and Molecular Behaviour", Van Nostrand Reinhold, London (1969)

21 Kaatzé, U., "The Dielectric Properties of Water in Its Different States of Interaction", Journal of Solution Chemistry, 26(1997)1049-1112

other, and these electrostatic interactions influence the ion-solvent interactions.

Equation (6.25) shows that the Helmholtz energy is lower in a medium of high relative permittivity, ϵ_r . The solvation energy is therefore negative if the ion is transferred from vacuum to a solvent.

By multiplying the energy in equation (6.25) with Avogadro's number, the Helmholtz energy of one mol of ions with charge Z_i is calculated. It is often of interest to know the change in Helmholtz energy when one mole of an ion is moved from a medium with one permittivity to a medium with another permittivity. This is the Helmholtz energy of transfer. If one mole of ions is moved from vacuum to a medium of relative permittivity ϵ_r , the energy change can be calculated as:

$$\Delta_{solv}A = \frac{Z_i^2 e^2 N_A}{8\pi\epsilon_0\epsilon_r r_i} - \frac{Z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} = \frac{Z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} \left(\frac{1}{\epsilon_r} - 1 \right) \quad (6.26)$$

It has been found that equation (6.26) gives very accurate results compared to experimental values of the solvation energy. An effective radius corresponding to the radius of the spherical cavity in the solvent created by an ion should be used in equation (6.26) [22, 23] rather than the ionic radius of the ion. According to Rashin and Honig [23], the radius of the cavity produced by the same ion is different in different solvents. When the Helmholtz energy of transfer between two solvents is calculated it is therefore necessary to use two different radii for the same ion. Besides, Rashin and Honig [23] found that the cavity radius of anions in water can be calculated by adding 7% to their ionic radius, while the cavity radius of cations can be calculated by adding 7 % to their covalent radius.

The covalent radius is half the distance between two identical atoms bonded together by a single covalent bond. The covalent radius of a metal cation is usually larger than the ionic radius but smaller than the atomic radius of the corresponding metal. The atomic radius of sodium is 190 pm, while the covalent radius of sodium is 154 pm and the ionic radius of the sodium ion is 102 pm. The argument for using the covalent radius of the metal rather than the ionic radius of the cation is that the covalent radius corresponds to the radius of the empty orbital around the cation. This empty orbital is assumed to form a part of the cavity.

For the transfer of one mole of ion i from a medium with relative permittivity $\epsilon_{r,1}$ to a medium with relative permittivity $\epsilon_{r,2}$, the Helmholtz energy of transfer is according to Rashin and Honig [23]:

$$\begin{aligned} \Delta_{transfer}A &= \frac{Z_i^2 e^2 N_A}{8\pi\epsilon_0 r_{i,2}} \left(\frac{1}{\epsilon_{r,2}} - 1 \right) - \frac{Z_i^2 e^2 N_A}{8\pi\epsilon_0 r_{i,1}} \left(\frac{1}{\epsilon_{r,1}} - 1 \right) \\ &= \frac{Z_i^2 e^2 N_A}{8\pi\epsilon_0} \left(\frac{1}{r_{i,2}\epsilon_{r,2}} - \frac{1}{r_{i,2}} - \frac{1}{r_{i,1}\epsilon_{r,1}} + \frac{1}{r_{i,1}} \right) \end{aligned} \quad (6.27)$$

The radii of the solvent cavities are marked with subscript 1 and 2 for the two solvents.

The Born term in equation (6.26) is often used with equations of state for electrolyte

22 Latimer W.M, Pitzer K.S., and Slansky C.M., "The Free Energy of Hydration of Gaseous Ions, and the Absolute Potential of the Normal Calomel Electrode", J. Am. Chem. Soc., 7(1939)108-111

23 Rashin A.A. and Honig B., "Reevaluation of the Born model of ion hydration", J. Physical Chemistry, 89(1985)5588-5593

solutions. In this case, the Born term contributes to the activity coefficients because of the variation of the relative permittivity with pressure. The Born term is also used for calculating the Gibbs energy of transfer. This is the difference in standard state chemical potential for a solute in two solvents with different relative permittivities. It is usually assumed that the Helmholtz energy difference calculated with equation (6.26) is identical to the corresponding difference in Gibbs energy.

The Helmholtz energy calculated from equation (6.25) is the difference in Helmholtz energy of a charged particle in a dielectric medium compared to the Helmholtz energy of an uncharged particle of the same size, in the same medium. The equation thus represents the contribution to the excess Helmholtz energy from the interaction between a single ion and a number of solvent molecules.

Helgeson *et al.* [24] used the equation of Born (6.25) in combination with the extended Debye-Hückel law (6.16) to derive an activity coefficient model. This activity coefficient model is identical to the one derived by Hückel [18] in 1925, but was derived on different theoretical assumptions. The Helgeson-Kirkham-Flowers model [24] can thus be seen as a more modern validation of Hückel's equation.

Exercise 6.4

According to Hefter *et al.* [25] the enthalpy of transfer of one mol of sodium chloride from pure water to pure methanol is -13000 J/mol and the corresponding entropy of transfer is -121 J/(mol·K) both at 298.15 K. The ionic radius of the chloride ion is 181 picometer and the covalent radius of sodium is 154 picometer. The relative permittivity of water is 78.48 and the relative permittivity of methanol is 32.66 at 298.15 K, both according to Albright and Gosting [26]. Calculate the Gibbs energy of transfer for one mole of sodium chloride being transferred from pure water to pure methanol at 25 °C. Assume that the cavity radii in water are the above radii plus 7 % and calculate the corresponding percentage that should be added to these radii in order to get the cavity radii in methanol. Why are the cavity radii larger in methanol than in water?

6.1.6 The mean spherical approximation

The Mean Spherical Approximation [27] uses a more “modern” method of calculating the excess Helmholtz energy from the electrostatic interactions than Debye and Hückel used [16]. The resulting MSA term seems to be more complicated than the corresponding Debye-Hückel term, but give similar numerical results. It was stated by Zuckerman *et al.* [28] that “At a purely theoretical level, however, one cannot be content since, *a priori*, there seem no clear grounds for preferring the DH-based theories—apart from their more direct and

24 Helgeson H.C., D.H. Kirkham, G.C. Flowers “Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures: IV. Calculation of Activity Coefficients, Osmotic Coefficients, and Apparent Molal and Standard and Relative Partial Molal Properties to 600°C and 5kb”, *American Journal of Science*, 281(1981)1249-1516

25 Hefter G., Marcus Y., and Waghorne W.E., “Enthalpies and Entropies of Transfer of Electrolytes and Ions from Water to Mixed Aqueous Organic Solvents”, *Chemical Reviews*, 8(2002)2773-2836

26 Albright P.S. and Gosting L.J., “Dielectric Constants of the Methanol-Water System from 5 to 55° C”, *J. Am. Chem. Soc.* 68(1946)1061-1063

27 Lebowitz J.L. and Percus J.K., “Mean Spherical Model for Lattice Gases with Extended Hard Cores and Continuum Fluids”, *Physical Review*, 144(1966)251-258

28 Zuckerman D.M., Fisher M.E., and Lee B.P., “Critique of primitive model electrolyte theories”, *Physical Review E*, 56(1997)6569-6580.

intuitive physical interpretation—rather than the more modern (and fashionable) MSA-based theories which—since they entail the pair correlation functions and the Ornstein-Zernike (OZ) relation—give the impression of being more firmly rooted in statistical mechanics. On the other hand, it has recently been shown that the DH theories yield pair correlations satisfying the OZ relation in a very natural way. Furthermore, both theories have an essentially meanfield character despite which, in contrast to typical mean field theories for lattice systems, neither has any known Gibbs-Bogoliubov variational formulation or similar basis. How, then, might the two approaches be distinguished?”

The derivation of the MSA term for electrostatic interactions is too complex for these notes. The interested reader is referred to papers like Lebowitz and Percus, “Mean Spherical Model for Lattice Gases with Extended Hard Cores and Continuum Fluids”[27].

The MSA expression for the Helmholtz energy of an electrolyte solution is according to Harvey et al.[29]:

$$A^E = -\frac{Ve^2}{4\pi\epsilon_0\epsilon} \left\{ \Gamma \sum_{ions} \frac{\rho_i z_i^2}{1 + \Gamma \sigma_i} + \frac{\pi}{2\Theta} \Omega P_n^2 \right\} + \frac{V\Gamma}{3\pi} kT \quad (6.28)$$

The terms in this equation are:

$$\Omega = 1 + \frac{\pi}{2\Theta} \sum_{ions} \frac{\rho_i \sigma_i^3}{1 + \Gamma \sigma_i}, \quad P_n = \frac{1}{\Omega} \sum_{ions} \frac{\rho_i \sigma_i z_i}{1 + \Gamma \sigma_i},$$

$$\Gamma = \frac{e}{2\sqrt{\epsilon_0\epsilon}kT} \left\{ \sum_i \rho_i \left(\left(z_i - \frac{\pi \sigma_i^2 P_n}{2\Theta} \right) / (1 + \Gamma \sigma_i) \right)^2 \right\}^{1/2} \quad (6.29)$$

$$\text{and } \Theta = 1 - \frac{\pi}{6} \sum_{ions} \rho_i \sigma_i^3, \quad \rho_i = \frac{N_i}{V} \text{ (number density of species } i)$$

In this form of the MSA term the MSA screening parameter, Γ is given with an implicit expression. By using an average diameter σ of the ions in the solution, the expression can be reduced to a simpler, explicit form:

$$A^E = -\frac{2\Gamma^3 RTV}{3\pi N_A} \left\{ 1 + \frac{3}{2} \Gamma \sigma \right\}$$

$$\sigma = \sum_{ions} n_i \sigma_i / \sum_{ions} n_i,$$

$$\Gamma = \frac{1}{2\sigma} \left[\sqrt{1 + 2\sigma\kappa} - 1 \right] \quad (6.30)$$

$$\kappa = \left(\frac{e^2 N_A^2}{\epsilon_r \epsilon_0 RTV} \sum_{ions} n_i Z_i^2 \right)^{1/2}$$

The expression for κ is identical to the expression used in Debye-Hückel theory, equation (6.6). The MSA term for electrostatic interactions is the preferred term for many researchers

29 Harvey A.H., Copeman T.W., and Prausnitz J.M. “Explicit Approximations to the Mean Spherical Approximation for Electrolyte Systems with Unequal Ion Sizes” J. Phys. Chem. 92(1988)6432-6436

attempting to develop equations of state for electrolytes. It was shown by Yi Lin [30] by Taylor expansion that there is virtually no difference between the MSA term and the Debye-Hückel term resulting from similar simplification of the two theories.

6.2 Empirical models for intermediate/short range interactions

The theory presented by Debye and Hückel was only meant to take the electrostatic interactions between spherical ions into account. The equations presented in the previous section for the mean spherical approximation are also limited to the electrostatic interactions between spherical ions. These equations therefore have to be combined with models or equations that describe other types of interactions such as ion-dipole and dipole-dipole interactions and short range interactions in order to be used for real solutions. Models for dipole-dipole interactions will not be considered further in these notes.

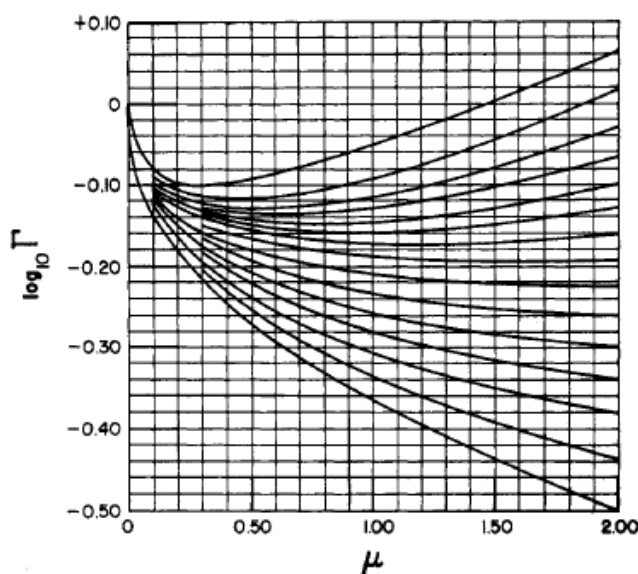


Figure 6.4: The logarithm of the reduced activity coefficient Γ versus ionic strength μ over the ionic strength range from 1 to 2 molal.

6.2.1 The Meissner correlation

In 1972 H.P. Meissner et al. started publication of a series of papers on activity coefficients of strong electrolytes in aqueous solutions [31,32]. The basis for their method was the observation that curves of the reduced activity coefficient, Γ , versus the ionic strength, I , for different salts form a family of curves that did not cross each other. This only applies to curves of the reduced activity coefficient, not to curves of mean ionic activity coefficients. One of the graphs presented in [31] is reproduced in Figure 6.4. It was pointed out one year later by Bromley [33] that Meissner had painted an idealized picture of electrolyte behavior and that some of the curves for common salts actually do cross each other.

The reduced activity coefficient, Γ , for a salt S was defined via the following equation:

$$\Gamma \equiv (\gamma_{\pm}^m)^{\frac{1}{|Z_C Z_A|}} \quad \text{or} \quad \gamma_{\pm}^m = \Gamma^{|Z_C Z_A|} \quad (6.31)$$

Initially, the method of Meissner and Tester [31] was a graphical method for determining activity coefficients in binary solutions using graphs like the one shown in Figure 6.4 valid

30 Lin Y. "Development of Equation of State for Electrolytes", Ph.D. thesis, Technical University of Denmark, 2008

31 Meissner H.P and Tester J.W., "Activity Coefficients of Strong Electrolytes in Aqueous Solution", Ind. Eng. Chem. Process Design and Development, 11(1972)128-133

32 Meissner H.P., Kusik C.L. "Activity Coefficients of Strong Electrolytes in Multicomponent Aqueous Solution", AIChE Journal, 18(1972)294-298

33 Bromley, L. A, "Thermodynamic properties of strong electrolytes in aqueous solutions", AIChE Journal 19(1973)313-320

up to two molal or valid up to 20 molal. Meissner and Kusik [32] showed how activity coefficients for multi component solutions could be calculated from the activity coefficients from binary solutions. In a solution of the three ions, 1, 2 and 3, which could represent Na^+ , Cl^- , and K^+ the reduced activity coefficient of electrolyte 12 (one-two) in the solution is given as a function of the reduced activity coefficients of the binary solutions of electrolyte 12 and 32 by:

$$\ln \Gamma_{12} = \ln \Gamma_{12}^0 + \frac{1}{2} X_3 \ln \frac{\Gamma_{32}^0}{\Gamma_{12}^0} \quad (6.32)$$

The reduced activity coefficients of binary solutions are indicated with superscript 0. The fraction X_3 is given by:

$$X_3 = \frac{m_3 Z_3^2}{m_1 Z_1^2 + m_3 Z_3^2} \quad (6.33)$$

Similar methods were given [32] for the calculation of reduced activity coefficients in solutions containing four or more ions.

Kusik and Meissner presented in 1978 [34] a set of equations for computer application of the method for calculating the reduced activity coefficients for binary solutions.

The value of the reduced activity coefficient Γ is calculated as:

$$\Gamma = [1 + B(1 + 0.1 \cdot I)^q - B] \Gamma^* \quad (6.34)$$

In this equation,

$$B = 0.75 - 0.065q \quad (6.35)$$

$$\log_{10} \Gamma^* = - \frac{0.5107 \sqrt{I}}{1 + C \sqrt{I}} \quad (6.36)$$

$$C = 1 + 0.055q \exp(-0.023 \cdot I^3) \quad (6.37)$$

The parameter q , Meissner's parameter, is dependent on the type of salt and of temperature. Each of the curves in Figure 6.4 corresponds to a different value of the q parameter.

If one experimental value of the activity coefficient is known, it is possible to identify which curve the electrolyte belongs to, and what q parameter is associated with the curve. Using the q parameter, the value of the activity coefficient at other concentrations and temperatures can then be predicted. Kusik and Meissner presented values of the q parameter for about 120 salts. Some of these parameters are shown in Table 6.1.

The q parameter is temperature dependent according to:

$$q_t = q + (aq + b) \cdot (t - 25) \quad (6.38)$$

The temperature t is in $^{\circ}\text{C}$. The parameter a has the value -0.0079, b has the value -0.0029 for sulfates (except sulfuric acid!). For most other electrolytes a is about -0.005 while b has the value 0.0085.

The Meissner method includes a graphical method for calculating water activities and a method for calculating mean ionic activity coefficients in multi-ion solutions. The reader is referred to the paper by Kusik and Meissner (1978) [34]. In spite of the resemblance between one of the terms in the Meissner correlation and the extended Debye-Hückel law, the

34 Kusik, C. L., Meissner, H. P. "Electrolyte activity coefficients in inorganic processing", AIChE Symp. Ser. 173, vol. 74(1978)14-20.

Meissner correlation is an empirical model. The Meissner correlation is also a predictive model and can be recommended for electrolytes for which only a few experimental data is available.

Table 6.1: Meissner's q parameters valid at 25°C

Electrolyte	Q	Electrolyte	Q
HCl	6.69	K ₂ SO ₄	-0.25
HNO ₃	3.66	Na ₂ SO ₄	-0.19
KBr	1.15	CaCl ₂	2.40
KCl	0.92	Mg(NO ₃) ₂	2.32
KNO ₃	-2.33	MgSO ₄	0.15
NaBr	2.98	Al ₂ (SO ₄) ₃	0.36
NaCl	2.23		
NaNO ₃	-0.39		
NH ₄ Cl	0.82		

Exercise 6.5

Calculate the solid-liquid equilibrium phase diagram for the ternary NaCl-KCl-H₂O system at 25 °C using Meissner's method. Compare the results with experimental values. Experimental values for the molalities of saturated solutions: (m_{NaCl}, m_{KCl}) = (0.0, 4.793), (1.353, 3.959), (2.828, 3.176), (5.154, 2.19), (5.716, 0.8151), (6.13, 0.0).

6.2.2 Bromley's method

In 1935 Guggenheim [35] suggested that the factor Ba in Hückel's equation (6.23) was set equal to 1. In 1973 L.A. Bromley [33] suggested a model based on a modification of "Guggenheim's equation", which was actually Hückels equation with $Ba=1$. Bromley's equation is given by:

$$\ln \gamma_{\pm}^m = -|Z_C Z_A| \frac{A\sqrt{I}}{1 + \sqrt{I}} + C_{CA} I \quad (6.39)$$

Compared to Hückel's equation (6.23), Bromley thus replaces γ_{\pm}^* with γ_{\pm}^m without any explanation and without any attempt to perform a correct conversion between the two types of activity coefficients. Besides, he proposes for C_{CA} :

$$\frac{C_{CA}}{\ln 10} = \frac{(0.06 + 0.6B_{CA})|Z_C Z_A|}{\left(1 + \frac{1.5}{|Z_C Z_A|} I\right)^2} + B_{CA} \quad (6.40)$$

The water activity according to the Bromley model is given as an expression for $1-\Phi$:

$$1 - \Phi = |Z_C Z_A| \frac{AI^{1/2}}{3} \sigma(I^{1/2}) - \ln(10) \cdot \left[(0.06 + 0.6B_{CA}) \frac{|Z_C Z_A|}{2} I \psi(aI) + \frac{B_{CA} I}{2} \right] \quad (6.41)$$

The parameter "a" is calculated from $a = 1.5/|Z_A Z_C|$. The function ψ is given by:

35 Guggenheim E.A., "The Specific Thermodynamic Properties of Aqueous Solutions of Strong Electrolytes" Philosophical Magazine, 19(1935)588-643

$$\psi(x) = \frac{2}{x} \left[\frac{1+2x}{(1+x)^2} - \frac{\ln(1+x)}{x} \right] \quad (6.42)$$

The function $\sigma(x)$ in equation (6.41) is identical to the function given in connection with the water activity coefficient according to the extended Debye-Hückel law in equation (6.19).

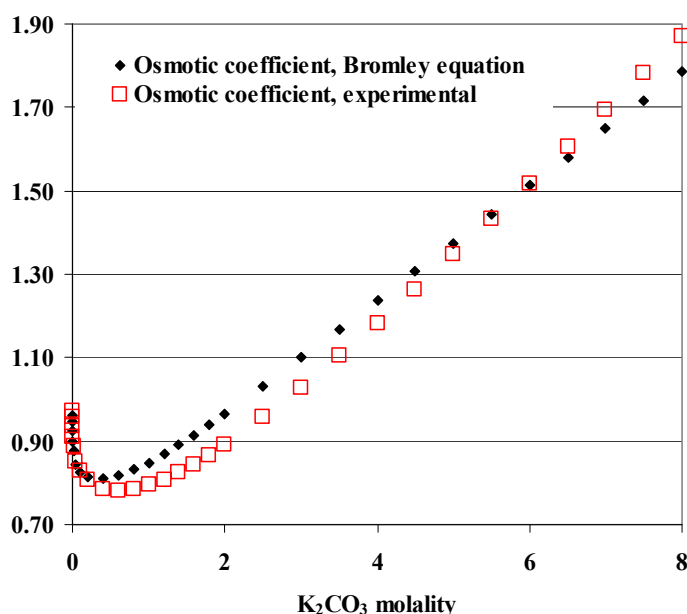


Figure 6.5: Osmotic coefficient for K_2CO_3 calculated with the Bromley equation and compared with experimental data. Bromley's equation is considered valid up to 6 molal and only at 25 °C.

Table 6.2: Bromley interaction parameters

Electrolyte	B_{CA} in kg/mol
HCl	0.1433
HNO ₃	0.0776
KBr	0.0296
KCl	0.024
KNO ₃	-0.0862
NaBr	0.0749
NaCl	0.0574
NaNO ₃	-0.0128
NH ₄ Cl	0.0200
H ₂ SO ₄	0.0606
K ₂ CO ₃	0.0372
K ₂ SO ₄	-0.0320
Na ₂ CO ₃	0.0089
Na ₂ SO ₄	-0.0204
CaCl ₂	0.0948
Mg(NO ₃) ₂	0.1014
MgSO ₄	-0.0153
Al ₂ (SO ₄) ₃	-0.0044

Bromley gave about 180 B_{CA} values valid at ionic strengths up to 6 mol/kg. Some of these values are shown in Table 6.2. The Bromley parameters are only valid at 25 °C. Bromley suggested an equation for the temperature dependence of the B_{CA} parameters in which each B_{CA} parameter is a function of four other parameters and the temperature. These four parameters need to be determined from experimental data at different temperatures.

Osmotic coefficients for K_2CO_3 calculated with Bromley's equation and compared with experimental data from Roy et al. [36] are shown in Figure 6.5. Bromley's parameters are valid up to 6 molal, and the figure shows a relatively good agreement between calculated and experimental data.

Bromley also suggested that the B_{CA} values may be calculated from ion specific parameters:

$$B_{CA} = B_C + B_A + \delta_C \delta_A \quad (6.43)$$

Some of the approximately 80 ion specific values given by Bromley are shown in Table 6.3. These values should only be used if the salt specific parameters are not available.

Bromley's model can be used for calculating activity coefficients in multi-component

36 Roy R.N., Gibbons J.J., Williams R., Godwin L., Baker G., Simonson J.M, Pitzer K.S., "The Thermodynamics of Aqueous Carbonate Solutions", J. Chem. Thermodynamics, 16(1984)303-315

solutions. The mean molal activity coefficient for a multi component solution is according to Bromley given by:

$$\ln \gamma_{\pm}^m = -\frac{1}{\nu} \sum v_i Z_i^2 \frac{A\sqrt{I}}{1+\sqrt{I}} + \frac{1}{\nu} \sum v_i F_i \quad (6.44)$$

For the cation C , F_i is given by:

$$F_C = \sum_{\text{Anions}} C_{C_i} \left(0.5 \cdot (Z_C + |Z_{A_i}|) \right)^2 m_{A_i} \quad (6.45)$$

For the anion A , the corresponding expression for F_i is:

$$F_A = \sum_{\text{Cations}} C_{C_i} \left(0.5 \cdot (Z_{C_i} + |Z_A|) \right)^2 m_{C_i} \quad (6.46)$$

Bromley's model has been widely used and is still being used. In a recent work, the Bromley model was used as part of a model to predict the formation of gas hydrates [37].

Table 6.3: Bromley ion specific parameters

Cation	B _C	δ _C	Anion	B _A	δ _A
H ⁺	0.0875	0.103	Cl ⁻	0.0643	-0.067
Na ⁺	0.0000	0.028	NO ₃ ⁻	-0.025	0.27
K ⁺	-0.0452	-0.079	SO ₄ ⁻²	0.000	-0.40
NH ₄ ⁺	-0.042	-0.02	CO ₃ ⁻²	0.028	-0.67
Ca ⁺²	0.0374	0.119			
Al ⁺³	0.052	0.12			

6.2.3 The Pitzer method

In 1973 K.S. Pitzer *et al.* presented the first of a long series of papers concerning the description of aqueous electrolyte solutions [38]. Pitzer used a particular definition of the ideal solution. The total Gibbs energy of an ideal solution according to Pitzer is given by:

$$G^{id} = n_w(\mu_w^0 - RTM_w\nu m_s) + n_s \sum v_i(\mu_i^m + RT \ln m_i) \quad (6.47)$$

The term for water in this definition of the ideal solution is different from the term obtained from the pure component standard state for water. If the pure component standard state was used for water and the standard state of the hypothetical ideal solution at unit molality was used for ions, the expression for the Gibbs energy of an ideal solution would be:

$$G^{id} = n_w(\mu_w^0 + RT \ln x_w) + n_s \sum v_i(\mu_i^m + RT \ln m_i) \quad (6.48)$$

According to equation (5.23), the value of $\ln x_w$ is approximately $-M_w\nu m_s$ at high dilution, which explains the use of that particular term in equation (6.47).

The total Gibbs energy of a solution of salts expressed with molal activity coefficients of solutes is given by:

$$G = n_w(\mu_w^0 + RT \ln(x_w\gamma_w)) + n_s \sum v_i(\mu_i^m + RT \ln(m_i\gamma_i^m)) \quad (6.49)$$

By inserting the definition of the osmotic coefficient from equation (5.18) this expression can

37 Jager M.D., Ballard, A.L.; Sloan Jr., E.D., "The next generation of hydrate prediction : II. Dedicated aqueous phase fugacity model for hydrate prediction", *Fluid Phase Equilibria*, 211(2003)85-107

38 K.S. Pitzer, *Activity Coefficients in Electrolyte Solutions*, 2nd Ed., CRC Press, 1991.

be changed to:

$$G = n_w(\mu_w^0 - RT\Phi M_w \nu m_s) + n_s \sum \nu_i (\mu_i^m + RT \ln m_i \gamma_i^m) \quad (6.50)$$

The expression for the total excess Gibbs energy used in the Pitzer method is calculated as the difference between the total Gibbs energy of the real solution (6.50) and the ideal solution (6.47):

$$\frac{G^E}{RT} = \frac{G - G^{id}}{RT} = n_s \sum \nu_i (1 - \Phi + \ln \gamma_i^m) \quad (6.51)$$

Partial differentiation of this Gibbs excess function with respect to moles of water will not give the water activity coefficient but instead $M_w \nu m_s (1 - \Phi)$. By partial differentiation of (6.51) with respect to moles of ion i , the molal activity coefficient γ_i^m is obtained directly.

The activity coefficients are not equal to the partial molar derivatives of the Gibbs excess function because the particular definition of the ideal solution in equation (6.47) is used. If the definition of the ideal solution from equation (6.48) were used, the activity coefficients would also not be equal to the partial molar derivatives of the excess Gibbs function.

The analytical expression for the total excess Gibbs energy function used in the Pitzer method is

$$\frac{G^{ex}}{RT} = n_w M_w f(I) + n_w M_w \sum_i \sum_j m_i m_j \lambda_{ij}(I) + n_w M_w \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} + \dots \quad (6.52)$$

The term $f(I)$ is Pitzer's empirical modification of the Debye-Hückel Gibbs excess function³⁹. Obviously, some modification of the Debye-Hückel Gibbs excess function was necessary in order to fit it into the particular definition of the ideal solution used by Pitzer. According to Pitzer, the term "includes the Debye-Hückel limiting law, but is an empirical form chosen for empirical effectiveness"³⁸. This empirical modification is called the Pitzer-Debye-Hückel term and has the form:

$$f(I) = -\frac{4}{3} A \frac{I}{b} \ln(1 + b\sqrt{I}) \quad (6.53)$$

The parameter $b = 1.2$. A is the Debye-Hückel parameter defined in Eq (6.13). The remaining terms in the Pitzer excess Gibbs energy function are empirical, virial expansion terms in molality. The second virial coefficient λ_{ij} is a function of ionic strength. The second virial coefficient is a parameter for the short range interactions between pairs of ions. Higher order virial coefficients are considered independent of ionic strength. The third virial coefficient is a parameter for the short range interaction between triplets of ions. This parameter is used for cation-anion-anion and cation-cation-anion interactions. Cation-cation-cation interactions and anion-anion-anion interactions are neglected.

The equation for the mean molal activity coefficient can be written in the following way for a single electrolyte according to Pitzer:

$$\ln \gamma_{\pm}^m = |Z_C Z_A| f^\gamma + m_s \left[\frac{2\nu_C \nu_A}{\nu} \right] B_{\pm}^\gamma + m_s^2 \left[\frac{2(\nu_C \nu_A)^{1.5}}{\nu} \right] C_{\pm}^\gamma \quad (6.54)$$

The term $|Z_C Z_A| f^\gamma$ is the contribution of the Pitzer Debye-Hückel term to the mean molal activity coefficient:

39 Pitzer K.S., Electrolytes. From dilute solutions to Fused Salts, J. Am. Chem. Soc. 102(1980)2902-6

$$f^\gamma = -\frac{A}{3} \left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b} \ln(1+b\sqrt{I}) \right] \quad (6.55)$$

The parameter $b = 1.2$. A is the Debye-Hückel parameter defined in Eq (6.13). $C_\pm^\gamma = \frac{3}{2} C_\pm^\Phi$. C_\pm^Φ is an adjustable parameter in the model.

The equation for B_\pm^γ is:

$$B_\pm^\gamma = 2\beta_0 + \frac{2\beta_1}{\alpha^2 I} \left(1 - (1 + \alpha\sqrt{I} - 0.5\alpha^2 I) \exp(-\alpha\sqrt{I}) \right) \quad (6.56)$$

In this equation, $\alpha = 2.0$. The two parameters β_0 and β_1 are adjustable parameters in the model.

For a 2-2 electrolyte the expression for B_\pm^γ is slightly different:

$$B_\pm^\gamma = 2\beta_0 + \frac{2\beta_1}{\alpha_1^2 I} \left(1 - (1 + \alpha_1\sqrt{I} - 0.5\alpha_1^2 I) \exp(-\alpha_1\sqrt{I}) \right) + \frac{2\beta_2}{\alpha_2^2 I} \left(1 - (1 + \alpha_2\sqrt{I} - 0.5\alpha_2^2 I) \exp(-\alpha_2\sqrt{I}) \right) \quad (6.57)$$

In this equation, $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$, β_2 is another adjustable parameter in the model.

The equation for the water activity coefficient is given by Pitzer as an equation for $\Phi-1$:

$$\Phi-1 = |Z_c Z_a| f^\Phi + m_s \frac{2\nu_c \nu_a}{\nu} B_\pm^\Phi + m_s^2 \frac{2(\nu_c \nu_a)^{3/2}}{\nu} C_\pm^\Phi \quad (6.58)$$

In this equation, f^Φ is the Pitzer-Debye-Hückel expression for the osmotic coefficient:

$$f^\Phi = -\frac{A}{3} \frac{\sqrt{I}}{1+b\sqrt{I}} \quad (6.59)$$

The expression for B_\pm^Φ is:

$$B_\pm^\Phi = \beta_0 + \beta_1 \exp(-\alpha\sqrt{I}) \quad (6.60)$$

In solutions with 2-2 salts, one more parameter is used in the expression for B_\pm^Φ :

$$B_\pm^\Phi = \beta_0 + \beta_1 \exp(-\alpha_2\sqrt{I}) + \beta_2 \exp(-\alpha_2\sqrt{I}) \quad (6.61)$$

The values of β_0 , β_1 , β_2 and C_\pm^Φ can be determined from experimental data. Pitzer et al. have published many such parameters. Some of these are shown in Table 6.4. Pitzers method can generally be used up to an ionic strength of 6.0 molal.

To use these equations one needs not only the previously mentioned β_0 , β_1 , β_2 and C_\pm^Φ parameters for the cation-anion (c-a) interaction but also parameters for c-c, a-a, a-a-c, and c-c-a interactions. The equations and parameters can for example be found in the book by Pitzer (1991) [38].

For calculations at temperatures different from 25 °C it is necessary to know the temperature dependence of each of the parameters. If sufficient experimental data are available, this

temperature dependence can be determined from experimental data. Ananthaswamy and Atkinson [40] used 6 virial coefficients to describe the binary $\text{CaCl}_2 - \text{H}_2\text{O}$ system up to 9.0 molal in the temperature range from 0 to 100 °C. The temperature dependences of each of the 6 virial coefficients were fitted to empirical functions of temperature. The number of parameters necessary to represent this binary system in a limited concentration range and a limited temperature range was 40.

The Pitzer method is primarily of academic interest. The number of parameters in the model is unlimited. The equations for multi component systems were not presented here because of the size of the expressions. The usual way to apply the Pitzer method to a specific binary or multi component system is to first use equations similar to those presented here. If the differences between experimental and calculated values are not satisfactory, additional parameters are added. The Pitzer method is often used to correlate experimental data when these are published. Modifications of the method are often used in review articles where it is attempted to correlate large amounts of published experimental data for a specific system. One such example is a work by Donald D. Archer [41] to describe the properties of sodium nitrate solutions by correlating previously published experimental data using an extension of the Pitzer equation. Another example is the previously mentioned work of Ananthaswamy and Atkinson [40].

Table 6.4: Pitzer parameters valid at 25 °C for binary solutions of one salt in water

Electrolyte	β_0	β_1		C_{\pm}^{Φ}
HCl	0.1775	0.2945		0.00080
HNO ₃	0.1168	0.3546		-0.00539
KBr	0.0569	0.2212		-0.00180
KCl	0.04835	0.2122		-0.00084
KNO ₃	-0.0816	0.0494		0.00660
NaBr	0.0973	0.2791		0.00116
NaCl	0.0765	0.2664		0.00127
NaNO ₃	0.0068	0.1783		-0.00072
NH ₄ Cl	0.0522	0.1918		-0.00301
	$4/3 \beta_0$	$4/3 \beta_1$		$2/3 2^{5/2} C_{\pm}^{\Phi}$
K ₂ SO ₄	0.0666	1.039		-
Na ₂ CO ₃	0.0483	2.013		0.0098
Na ₂ SO ₄	0.0249	1.466		0.010463
	β_0	β_1	β_2	C_{\pm}^{Φ}
CaSO ₄	0.20	3.197	-54.24	-
MgSO ₄	0.2210	3.343	-37.23	0.0250

Exercise 6.6

If the definition of the ideal solution in equation (6.48) is used, what are then the partial

40 Ananthaswamy J. and G. Atkinson, "Thermodynamics of Concentrated Electrolyte Mixtures 5. A Review of the Properties of Aqueous Calcium Chloride in the Temperature Range 273.15-373.15K", J. Chem. Eng. Data, 30(1985)120-128

41 Archer D.G., "Thermodynamic properties of the $\text{NaNO}_3 + \text{H}_2\text{O}$ System", J. Phys. Chem. Ref. Data, 29(2000)1141-1116

molar derivatives of the excess Gibbs function with respect to mol water? Hint: Derive the corresponding excess Gibbs function and differentiate it with respect to moles of water. Use the Gibbs-Duhem equation to determine the derivatives of the activity coefficients with respect to mol water.

Exercise 6.7

Calculate the mean molal activity coefficients of NaCl solutions using the Pitzer-Debye-Hückel equation. Use the value of the Debye-Hückel parameter $A = 1.17165 \text{ (kg/mol)}^{1/2}$. Compare the results with the corresponding values calculated with the extended Debye-Hückel law by plotting the graphs. Use a value of $Ba = 1.5 \text{ (kg/mol)}^{1/2}$ in the extended Debye-Hückel law.

Calculate mean molal activity coefficients with the Pitzer equation at the concentrations for which experimental data are given in Table 5.3. Plot the experimental and calculated values in the same diagram to compare.

6.3 Intermediate/Short range interactions from local composition models

Local composition models are models based on the local composition concept introduced by Grant M. Wilson in 1964 [42]. It is assumed that the composition on a molecular level is different from the bulk composition. Depending on sizes, shapes, and interaction energies, molecules are preferentially surrounded by other molecules that give them a lower energy level. The Debye-Hückel theory can be considered to be a local composition theory for electrostatic interactions.

6.3.1 The Extended UNIQUAC model

Sander et al. [43] presented in 1986 an extension of the UNIQUAC model by adding a Debye-Hückel term allowing this Extended UNIQUAC model to be used for electrolyte solutions. The model has since been modified and it has proven itself applicable for calculations of vapor-liquid-liquid-solid equilibria and of thermal properties in aqueous solutions containing electrolytes and non-electrolytes. The model is shown in its current form here as it is presented by Thomsen (1997) [44].

The extended UNIQUAC model consists of three terms: a combinatorial or entropic term, a residual or enthalpic term and an electrostatic term

$$G^{ex} = G_{Combinatorial}^{ex} + G_{Residual}^{ex} + G_{Extended\ Debye-H\ddot{u}ckel}^{ex} \quad (6.62)$$

The combinatorial and the residual terms are identical to the terms used in the traditional UNIQUAC equation [45, 46]. The electrostatic term corresponds to the extended Debye-Hückel law, given in equation (6.15).

The combinatorial, entropic term is independent of temperature and only depends on the

42 Wilson GM, "Vapor-Liquid Equilibrium XI. A New Expression for the Excess Free Energy of Mixing", J. Am. Chem. Soc., 86(1964)127-130

43 B. Sander; P. Rasmussen and Aa. Fredenslund, "Calculation of Solid-Liquid Equilibria in Aqueous Solutions of Nitrate Salts Using an Extended UNIQUAC Equation". Chemical Engineering Science, 41(1986)1197-1202

44 Thomsen, K., Aqueous electrolytes: model parameters and process simulation, Ph.D. Thesis, Department of Chemical Engineering, Technical University of Denmark, 1997.

45 Abrams D.S. and Prausnitz J.M., "Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems", AIChE journal 21(1975)116-128

46 Maurer G., Prausnitz J.M., "On the derivation and extension of the UNIQUAC equation", Fluid Phase Equilibria, 2(1978)91-99

relative sizes of the species:

$$\frac{G_{Combinatorial}^{ex}}{RT} = \sum_i x_i \ln \left(\frac{\phi_i}{x_i} \right) - \frac{z}{2} \sum_i q_i x_i \ln \left(\frac{\phi_i}{\theta_i} \right) \quad (6.63)$$

$z = 10$ is the co-ordination number. x_i is the mole fraction, ϕ_i is the volume fraction, and θ_i is the surface area fraction of component i :

$$\phi_i = \frac{x_i r_i}{\sum_l x_l r_l}; \quad \theta_i = \frac{x_i q_i}{\sum_l x_l q_l} \quad (6.64)$$

The two model parameters r_i and q_i are the volume and surface area parameters for component i . In the classical application of the UNIQUAC model, these parameters are calculated from the properties of non electrolyte molecules [45]. In the Extended UNIQUAC application to multi component electrolyte solutions, this approach gave unsatisfactory results. The volume and surface area parameters were instead considered to be adjustable parameters. The values of these two parameters are determined by fitting to experimental data. Especially thermal property data such as heat of dilution and heat capacity data are efficient for determining the value of the surface area parameter q , because the UNIQUAC contribution to the excess enthalpy and excess heat capacity is proportional to the parameter q .

The residual, enthalpic term is dependent on temperature through the parameter ψ_{kl} :

$$\frac{G_{Residual}^{ex}}{RT} = - \sum_i x_i q_i \ln \left(\sum_k \theta_k \psi_{ki} \right) \quad (6.65)$$

the parameter ψ_{kl} is given by:

$$\psi_{kl} = \exp \left(- \frac{u_{kl} - u_{ll}}{T} \right) \quad (6.66)$$

u_{kl} and u_{ll} are interaction energy parameters. The interaction energy parameters are considered symmetrical and temperature dependent in this model

$$u_{kl} = u_{kl}^0 + u_{kl}^T (T - 298.15) \quad (6.67)$$

The interaction parameters u_{kl}^0 and u_{kl}^T are model parameters that are fitted to experimental data.

By partial molar differentiation of the combinatorial and the residual UNIQUAC terms, the combinatorial and the residual parts of the rational, symmetrical activity coefficients are obtained:

$$\ln \gamma_i^C = \ln \left(\frac{\phi_i}{x_i} \right) + 1 - \frac{\phi_i}{x_i} - \frac{z}{2} q_i \left[\ln \left(\frac{\phi_i}{\theta_i} \right) + 1 - \frac{\phi_i}{\theta_i} \right] \quad (6.68)$$

$$\ln \gamma_i^R = q_i \left[1 - \ln \left(\sum_k \theta_k \psi_{ki} \right) - \sum_k \frac{\theta_k \psi_{ik}}{\sum_l \theta_l \psi_{lk}} \right]$$

The infinite dilution terms are obtained by setting $x_w = 1$ in equation (6.68).

$$\ln \gamma_i^{C\infty} = \ln \frac{r_i}{r_w} + 1 - \frac{r_i}{r_w} - \frac{z}{2} q_i \left[\ln \frac{r_i q_w}{r_w q_i} + 1 - \frac{r_i q_w}{r_w q_i} \right] \quad (6.69)$$

$$\ln \gamma_i^{R\infty} = q_i [1 - \ln \psi_{wi} - \psi_{iw}]$$

The combinatorial and the residual terms of the UNIQUAC excess Gibbs energy function are based on the rational, symmetrical activity coefficient convention. The Debye-Hückel electrostatic term however is expressed in terms of the rational, symmetrical convention for water, and the rational, unsymmetrical convention for ions.

The electrostatic contributions to the water activity coefficients and the ionic activity coefficients are obtained by partial molar differentiation of the extended Debye-Hückel law excess Gibbs energy term (6.15). The term used for water is slightly modified compared to equation (6.19) so that the parameter $b = 1.5 \text{ (kg/mol)}^{1/2}$ is used instead of the Ba term:

$$\ln \gamma_w^{DH} = \frac{2}{3} M_w A I^{3/2} \sigma (bI^{1/2}) \quad (6.70)$$

$$\sigma(x) = \frac{3}{x^3} \left\{ 1 + x - \frac{1}{1+x} - 2 \ln(1+x) \right\}$$

Also the term used for ions is slightly modified compared to equation (6.16) so that the parameter b replaces Ba :

$$\ln \gamma_i^{*DH} = -Z_i^2 \frac{A\sqrt{I}}{1+b\sqrt{I}} \quad (6.71)$$

Based on table values of the density d_o of pure water, and the relative permittivity of water, ϵ_r , the Debye-Hückel parameter A in equation (6.13) used in equation (6.70) and (6.71) can be approximated in the temperature range $273.15 \text{ K} < T < 383.15 \text{ K}$ by

$$A = [1.131 + 1.335 \cdot 10^{-3} (T - 273.15) + 1.164 \cdot 10^{-5} \cdot (T - 273.15)^2] (\text{kg/mol})^{1/2} \quad (6.72)$$

The activity coefficient for water is calculated in the Extended UNIQUAC model by summation of the three terms:

$$\ln \gamma_w = \ln \gamma_w^C + \ln \gamma_w^R + \ln \gamma_w^{DH} \quad (6.73)$$

The activity coefficient for ion i is obtained as the rational, unsymmetrical activity coefficient according to the definition of rational unsymmetrical activity coefficient in equation (4.7) by adding the three contributions:

$$\begin{aligned} \ln \gamma_i^* &= \ln \frac{\gamma_i^C}{\gamma_i^{C\infty}} + \ln \frac{\gamma_i^R}{\gamma_i^{R\infty}} + \ln \gamma_i^{*DH} \\ &= \ln \gamma_i^C - \ln \gamma_i^{C\infty} + \ln \gamma_i^R - \ln \gamma_i^{R\infty} + \ln \gamma_i^{*DH} \end{aligned} \quad (6.74)$$

The rational, unsymmetrical activity coefficient for ions calculated with the Extended UNIQUAC model can be converted to a molal activity coefficient by use of the definition in equation (4.11). This is relevant for comparison with experimental data.

Parameters for water and for the following ions can be found in Thomsen (1997) [44]: H^+ , Na^+ , K^+ , NH_4^+ , Cl^- , SO_4^{2-} , HSO_4^- , NO_3^- , OH^- , CO_3^{2-} , HCO_3^- , $\text{S}_2\text{O}_8^{2-}$.

Parameters and model modifications for gas solubility at pressures up to 100 bar in aqueous

electrolyte systems have later been published [47, 48]. Also phase equilibria for systems containing non-electrolytes are described by the model, including liquid-liquid equilibria [49, 50]. Besides, parameters have been determined for systems containing heavy metal ions [51].

The model has been applied by A.V. Garcia to include the pressure dependence of the solubility of salts. Two parameters for the pressure dependence of the solubility product of each salt were introduced in order to achieve this [52, 53].

A significant advantage of the Extended UNIQUAC model compared to models like the Bromley model or the Pitzer model is that temperature dependence is built into the model. This enables the model to also describe thermodynamic properties that are temperature derivatives of the excess Gibbs function, such as heat of mixing and heat capacity.

Exercise 6.8:

Show how the infinite dilution coefficients in (6.69) are derived from (6.68).

Exercise 6.9:

Read the paper in which the UNIQUAC equation was introduced by Abrams and Prausnitz [45]. Write a short resume of the paper.

6.3.2 The electrolyte NRTL model

The electrolyte NRTL model [54, 55, 56] combines the Pitzer-Debye-Hückel term with the NRTL local composition model [57]. The local composition concept is modified for ions and the model parameters are salt specific. The Extended UNIQUAC model is also a combination of a Debye-Hückel term and a local composition model. At first glance, the two models therefore seem to be similar. Some of the differences between the two models are listed in Table 6.5.

47 K. Thomsen and P. Rasmussen, "Modeling of Vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems" *Chemical Engineering Science* 54(1999)1787-1802

48 S. Pereda, K. Thomsen, P. Rasmussen "Vapor-Liquid-Solid Equilibria of Sulfur Dioxide in Aqueous Electrolyte Solutions" *Chemical Engineering Science* 55(2000)2663-2671

49 M. Iliuta, K. Thomsen, P. Rasmussen "Extended UNIQUAC model for correlation and prediction of vapor-liquid-solid equilibrium in aqueous salt systems containing non-electrolytes. Part A. Methanol – Water – Salt systems" *Chemical Engineering Science* 55(2000)2673-2686

50 K. Thomsen, M. Iliuta, P. Rasmussen "Extended UNIQUAC model for correlation and prediction of vapor-liquid-liquid-solid equilibria in aqueous salt systems containing non-electrolytes. Part B. Alcohol (Ethanol, Propanols, Butanols) - water - salt systems" *Chemical Engineering Science* 59(2004)3631-3647

51 Maria C. Iliuta, Kaj Thomsen, Peter Rasmussen "Modeling of heavy metal salt solubility using the extended UNIQUAC model" *AIChE Journal*, 48(2002)2664-2689

52 Ada Villafañila Garcia, Kaj Thomsen, Erling H. Stenby, "Prediction of mineral scale formation in geothermal and oilfield operations using the extended UNIQUAC model Part I. Sulfate scaling minerals" *Geothermics* 34(2005)61-97

53 Ada Villafañila Garcia, Kaj Thomsen, Erling H. Stenby, "Prediction of mineral scale formation in geothermal and oilfield operations using the extended UNIQUAC model Part II. Carbonate scaling minerals", *Geothermics*, 35(2006)239-284

54 C.C. Chen, H.I. Britt, J.F. Boston, L.B. Evans, "Local Composition Model for Excess Gibbs Energy of Electrolyte Systems" *AIChE Journal*, 28(1982)588-596

55 C.C. Chen and L.B. Evans, "A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems", *AIChE Journal* 32(1986)444-454.

56 C.C. Chen and Y. Song, "Generalized Electrolyte-NRTL Model for Mixed-Solvent Electrolyte Systems" *AIChE Journal* 50(2004)1928-1941.

57 Renon H., Prausnitz J.M., "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures", *AIChE Journal*, 14(1968)135-144

Table 6.5: Differences between the electrolyte NRTL model and the Extended UNIQUAC model.

Property	Model	
	Electrolyte NRTL model	Extended UNIQUAC model
Local composition term:	Modified NRTL	Standard UNIQUAC
Electrostatic term:	Pitzer-Debye-Hückel	Extended Debye-Hückel
Parameters:	Salt specific	Ion specific
Gibbs excess function	$G^E = H^E$	$G^E = H^E - TS^E$

The electrolyte NRTL model uses a local composition concept adapted to electrolyte solutions. The expressions for the activity coefficients are considerably more complicated and require more time for programming than those from the Extended UNIQUAC model [56]. The use of a Pitzer-Debye-Hückel term instead of the Extended Debye-Hückel term does not make much difference.

The NRTL local composition model only has an enthalpic term, it uses no volume and surface area fractions and has no entropic term.

The use of salt specific parameters rather than ion specific parameters requires that a suitable mixing rule is applied. Otherwise calculations of solution properties would depend on how the composition of the solution is defined. A solution of equal amounts of CaCl_2 and MgNO_3 could as well be defined as a solution of $\text{Ca}(\text{NO}_3)_2$ and MgCl_2 . The electrolyte NRTL model is widely used as it is the model implemented in the commercial simulator ASPEN [58].

The reader is referred to the original papers [54, 55, 56] for the relevant equations used in this model.

Exercise 6.10

Read the paper by Chen *et al.* [54] in which they introduced the electrolyte NRTL model. Write a short resume of the paper.

6.4 Intermediate/Short range interactions from equations of state

An equation of state provides an analytical relation between pressure, volume, and temperature (PVT). Polynomial equations that are cubic in molar volume are known as cubic equations of state. Cubic equations of state are the simplest equations capable of representing both liquid and vapor behavior. It is therefore possible to describe the intermediate/short range interactions in electrolyte solutions using a cubic or more advanced equation of state.

Local composition models such as the NRTL model and the UNIQUAC model are based on the assumption that the effect of pressure on these liquid mixtures is negligible. Equations of state include the effect of pressure and can possibly be used for calculating activity coefficients as function of pressure. This pressure dependence is important in a number of applications: The precipitation of salts during oil production and the production of geothermal energy is taking place due to changes in both temperature and pressure. This phenomenon is called scaling. A better description of this phenomenon might be achieved by models that include the effect of pressure, such as equations of state.

6.4.1 Fugacity coefficients and activity coefficients

Fugacity coefficients of components in a mixture, $\hat{\phi}_i$ are derived from equations of state in

58 <http://www.aspentech.com/>

order to perform vapor-liquid equilibrium calculations in systems that can be described with such equations. Fugacity coefficients describe the deviation of the properties of a real mixture from the properties of an ideal gas mixture.

Just like an ideal solution is defined by the chemical potentials of its components, an ideal gas mixture is defined by the chemical potentials of its components. The chemical potential of a component in an ideal gas mixture is:

$$\mu_i^{ig}(T, P) = \mu_i^{0,ig}(T, P) + RT \ln x_i \quad (6.75)$$

The mole fraction of component i in the ideal gas mixture is x_i . A superscript 0 is used to indicate the chemical potential of the pure ideal gas, which is obviously used as the standard state. The superscript ig indicates ideal gas. The chemical potentials of gases are sensitive to the pressure. The ideal gas standard state chemical potentials are usually given at 1 bar. A pressure of 1 bar will be denoted as P_0 . The chemical potential of pure gas i at the pressure P is:

$$\mu_i^{0,ig}(T, P) = \mu_i^{0,ig}(T, P_0) + RT \ln \frac{P}{P_0} \quad (6.76)$$

The chemical potential of component i in an ideal gas mixture at a pressure P is then according to equation (6.75):

$$\mu_i^{ig}(T, P) = \mu_i^{0,ig}(T, P_0) + RT \ln \frac{Px_i}{P_0} \quad (6.77)$$

The deviation from ideal gas behavior by a real solution at T, P is described by the term $RT \ln \hat{\phi}_i$. This term is called the residual term and corresponds to the excess term $RT \ln \gamma_i$ that describes the deviation from ideal solution behavior by a real solution. The chemical potential of component i in the real mixture is:

$$\mu_i(T, P) = \mu_i^{0,ig}(T, P_0) + RT \ln \frac{Px_i}{P_0} + RT \ln \hat{\phi}_i \quad (6.78)$$

The corresponding equation in the ideal solution reference system is:

$$\mu_i(T, P) = \mu_i^0(T, P_0) + V_i(P - P_0) + RT \ln(x_i \gamma_i) \quad (6.79)$$

The standard state chemical potential at T, P has here been calculated in the same way as it was done in equation (5.42).

The chemical potential has the same numerical value, no matter what reference system is used. Equations (6.78) and (6.79) are combined to give:

$$\mu_i^{0,ig}(T, P_0) + RT \ln \frac{P \hat{\phi}_i}{P_0} = \mu_i^0(T, P_0) + V_i(P - P_0) + RT \ln \gamma_i \quad (6.80)$$

In an ideal solution $\gamma_i = 1$ when the symmetrical convention is used and the corresponding equation is:

$$\mu_i^{0,ig}(T, P_0) + RT \ln \frac{P \hat{\phi}_i}{P_0} = \mu_i^0(T, P_0) + V_i(P - P_0) \quad (6.81)$$

If the solution only consists of the pure species i , the fugacity coefficient at T, P is ϕ_i , and the equation is:

$$\mu_i^{0,ig}(T, P_0) + RT \ln \frac{P\phi_i}{P_0} = \mu_i^0(T, P_0) + V_i(P - P_0) \quad (6.82)$$

Equation (6.82) is subtracted from equation (6.80) to give:

$$\ln \frac{P\hat{\phi}_i}{P_0} - \ln \frac{P\phi_i}{P_0} = \ln \gamma_i \quad \Rightarrow \quad \frac{\hat{\phi}_i}{\phi_i} = \gamma_i \quad (6.83)$$

The result is that the ratio between the fugacity coefficient of component i in a mixture and the fugacity of pure component i at the same temperature and pressure is equal to the activity coefficient of the component. This expression can be used for calculating activity coefficients from fugacity coefficients.

For the calculation of the rational, unsymmetrical activity coefficient, it is necessary to calculate the fugacity coefficient at infinite dilution in order to obtain the infinite dilution activity coefficient. The fugacity coefficient of solute i at infinite dilution, ϕ_i^∞ , is calculated at T, P from the equation of state from a composition vector consisting of water and no ions:

$$\frac{\hat{\phi}_i^\infty}{\phi_i} = \gamma_i^\infty \quad (6.84)$$

The unsymmetrical activity coefficient can therefore be calculated from

$$\gamma_i^* = \frac{\gamma_i}{\gamma_i^\infty} = \frac{\hat{\phi}_i / \phi_i}{\hat{\phi}_i^\infty / \phi_i} = \frac{\hat{\phi}_i}{\hat{\phi}_i^\infty} \quad (6.85)$$

Equations of state for electrolytes are still only considered of academic interest. Most equations of state for electrolytes can only be applied to binary systems at 25 °C. An engineering equation requires a high accuracy in phase equilibrium calculations for multi component solutions over a wide temperature range.

6.4.2 The Fürst and Renon equation of state

Fürst and Renon [59] based their equation of state for electrolytes on a non-electrolyte part from the equation of state of Schwartzentruber *et al.* [60], and an electrostatic part composed of an MSA long-range term, they also used an additional short range interaction term specific to ions. They applied their model to calculate osmotic coefficients of dilute binary and ternary solutions at 25°C. The model uses ion specific parameters.

6.4.3 The Wu and Prausnitz equation of state

Wu and Prausnitz [61] based their equation of state on the Peng-Robinson equation of state combined with an association term to account for hydrogen bonding, a Born term for the Helmholtz energy change of transferring an ion between phases, and an MSA term for the long range interactions between charges. The model was used for calculating vapor-liquid equilibrium in water-hydrocarbon mixtures with and without salt, mean ionic activity coefficients, and water activities (not osmotic coefficients) for binary aqueous salt solutions.

59 Fürst W., Renon H. "Representation of Excess Properties of Electrolyte Solutions Using a New Equation of State" *AIChE Journal* 39(1993)335-343.

60 Schwartzentruber J., Renon H., Watanasiri S., "Development of a New Cubic Equation of State for Phase Equilibrium Calculations", *Fluid Phase Equilibria*, 52(1989)127-134

61 Wu J. and Prausnitz J.M. "Phase Equilibria for Systems Containing Hydrocarbons, Water and Salt: An Extended Peng-Robinson Equation of State" *Ind. Eng. Chem. Res.* 37(1998)1634-1643

The model uses ion specific parameters and was applied in a wide temperature and pressure range.

6.4.4 The Myers-Sandler-Wood equation of state

The Myers-Sandler-Wood equation of state [62] combines the Peng-Robinson cubic equation of state with a Born term and the explicit MSA term (6.30). Salt specific parameters valid at 25°C for a number of salts in aqueous solutions were determined and it was shown that mean activity coefficients of ions and the osmotic coefficient could be calculated with reasonable accuracy at 25°C. For a few binary systems, temperature dependent parameters were determined and it was shown that experimental mean activity coefficients, osmotic coefficients and densities could be reproduced for those binary systems in a wide temperature range.

6.4.5 Comparative study of equations of state

In a comparative study, Yi Lin [30], examined the performance of four different equations of state for electrolytes. A test system consisting of the multi-component system $\text{H}_2\text{O} - (\text{Na}^+, \text{H}^+, \text{Ca}^{2+}) - (\text{Cl}^-, \text{OH}^-, \text{SO}_4^{2-})$ at 25 °C was used. The four equations of state were:

- The Myers-Sandler-Wood electrolyte equation of state with ion-specific parameters but otherwise identical to the model by Myers et al. [62] This model requires three ion-specific parameters in addition to interaction parameters for the interactions between each species pair. The three ion specific parameters are the attraction parameter a , the co-volume parameter b , and an ion size parameter σ for the MSA term.
- The Myers-Sandler-Wood electrolyte equation of state with ion-specific parameters and the explicit MSA term replaced with the implicit MSA term from (6.28). This equation of state uses the same number and the same types of parameters as the equation of state above.
- The Cubic Plus Association equation of state [63] for intermediate/short range interactions and the implicit MSA term for electrostatic interactions. This equation of state uses the same number and the same types of parameters as the equation of state above. This equation of state gives the option of adding association terms for the components. This option was only used for the self association of water.
- The Soave-Redlich-Kwong equation of state [64] for intermediate/short range interactions and the extended Debye-Hückel equation (6.16), (6.19) with $Ba = 1.5 (\text{kg/mol})^{1/2}$ for the electrostatic interactions. This equation has only two ion specific parameters. The two ion specific parameters are the attraction parameter a , and the co-volume parameter b .

Usually the parameters in equations of state such as the Peng-Robinson EOS are determined on the basis of the critical properties of the species. Critical properties do not exist for ions. These parameters were therefore considered adjustable parameters that could be determined

62 Myers J.A., S.I. Sandler, R.H. Wood "An Equation of State for Electrolyte Solutions Covering Wide Ranges of Temperature, Pressure and Composition" Ind. Eng. Chem. Res. 41(2002)3282-3297

63 Kontogeorgis G.M., Yakoumis I.V., Meijer H., Hendriks E., Moorwood T. "Multicomponent phase equilibrium calculations for water-methanol-alkane mixtures", Fluid Phase Equilib. 158-160(1999)201-209

64 Soave G. "Equilibrium constants from a modified Redlich-Kwong equation of state", Chemical Engineering Science, 27(1972)1197-1203

as the best fit to the experimental data.

The parameters in the models were determined on the basis of a databank consisting of 1300 experimental data points for the test system at 25 °C. The data consisted of

- Activity coefficients
- Osmotic coefficients
- Density data
- Solid-liquid equilibrium data

The difference between the performances of these four equations of state was remarkably low. The three first of the equations of state performed equally well with all four types of data. There was no significant difference between using the implicit MSA term and the simpler explicit MSA term. Also there was no difference between using the Cubic Plus Association equation of state for intermediate/short range interactions instead of the Peng-Robinson equation of state. Most surprisingly, the last of the four equations of state tested, performed equally well as the three first concerning activity coefficients, osmotic coefficients, and solid-liquid equilibrium data. This equation was however not able to reproduce density data with good accuracy. This can be explained by the fact that the extended Debye-Hückel term used for this equation of state does not contain a volume term.

From the point of view of computation time, the Soave-Redlich-Kwong equation of state combined with the extended Debye-Hückel term was the clear winner. The two models that used the implicit form of the MSA electrostatic term used 2.5 times the calculation time of the Myers-Sandler-Wood model with the explicit MSA term.

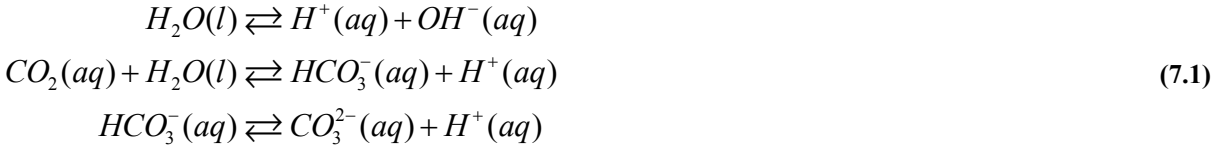
7 Equilibrium calculations

With a thermodynamic model for electrolyte solutions, it is possible to perform calculations of various properties of such solutions. The first type of calculation to perform is usually an equilibrium calculation to determine if the solution forms one homogeneous phase. First a speciation equilibrium calculation is performed in order to determine the degree of dissociation of the various electrolytes. Subsequently solid-liquid, vapor-liquid, or liquid-liquid equilibrium calculations are performed.

7.1 Speciation equilibrium

The term speciation is used to describe what happens when electrolytes are dissolved in water. Electrolytes dissociate partly or completely, hydrolyze and form complexes. The true composition of the solution is calculated by solving the equations for speciation equilibria. A speciation equilibrium calculation can be performed alone or simultaneous with a solid-liquid, vapor-liquid, or liquid-liquid equilibrium calculation.

If H_2O , $NaOH$, and CO_2 are mixed, various reactions will occur. A speciation equilibrium calculation will give the amounts of each species in the mixture at equilibrium. In this mixture, the amounts of H_2O , CO_2 , HCO_3^- , CO_3^{2-} , H^+ , Na^+ , and OH^- can be calculated in a speciation equilibrium calculation. Here it is first assumed that no solid precipitates and no gas phase forms. The following equilibria then have to be considered:



The condition for equilibrium is that the sum of the chemical potential of the reactants is equal to the sum of the chemical potentials of the products. This can be used to express these three chemical equilibria mathematically:

$$\begin{aligned} \mu_{H_2O(l)} &= \mu_{H^+(aq)} + \mu_{OH^-(aq)} \\ \mu_{CO_2(aq)} + \mu_{H_2O(l)} &= \mu_{HCO_3^-(aq)} + \mu_{H^+(aq)} \\ \mu_{HCO_3^-(aq)} &= \mu_{CO_3^{2-}(aq)} + \mu_{H^+(aq)} \end{aligned} \quad (7.2)$$

By use of equation (4.6) and (4.8) these chemical potentials can be expressed as functions of the standard state chemical potentials, the composition, and the activity coefficients. This is shown here for the first of the three equilibria in (7.2):

$$\mu_{H_2O(l)}^0 + RT \ln a_{H_2O} = \mu_{H^+(aq)}^* + RT \ln a_{H^+(aq)}^* + \mu_{OH^-(aq)}^* + RT \ln a_{OH^-(aq)}^* \quad (7.3)$$

The standard state chemical potentials are collected on the left hand side of the equation and the activities on the right hand side:

$$-\frac{\mu_{H^+(aq)}^* + \mu_{OH^-(aq)}^* - \mu_{H_2O(l)}^0}{RT} = \ln \frac{a_{H^+(aq)}^* a_{OH^-(aq)}^*}{a_{H_2O(l)}} \quad (7.4)$$

The standard state chemical potentials can be found in tables such as the NBS tables of

chemical thermodynamic properties [3,65]. The numerical value of the left hand side of the equation can thus be calculated. A model for the activity coefficients as functions of composition, temperature and pressure is required in order to solve equation (7.4). If such a model is available, the equation can be solved together with the two similar equations that can be written based on the two other equilibria in (7.2).

Equation (7.4) can be written in the following, maybe more familiar way:

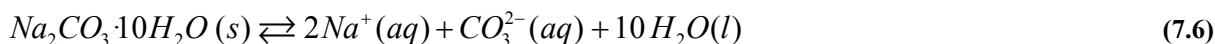
$$\ln K = -\frac{\Delta G^0}{RT} = \sum \ln a_i^{v_i} \quad (7.5)$$

In this equation K is the equilibrium constant. ΔG^0 is the increment in standard state Gibbs energy by the equilibrium corresponding to the numerator on the left hand side of equation (7.4), a_i is the activity, and v_i is the stoichiometric coefficient of component i , positive for products and negative for reactants. In equation (7.5) 0 is being used as superscript for the increment in standard state Gibbs energy. No superscript is being used for the activities. The equation can be used with symmetrical properties for water. For solutes, one of the three activity coefficient systems can be used together with the corresponding standard state properties.

After a speciation calculation is carried out it should be checked if one or more of the possible solid phases have a lower chemical potential than its components in solution. If this is the case, the solution is not stable and one or more solids will precipitate. Likewise a bubble point calculation can be carried out in order to determine if gases will evaporate from the solution and a liquid-liquid equilibrium calculation can be performed to see if the solution will split into more liquid phases.

7.2 Solid-liquid equilibrium

A number of different solids can form in an aqueous solution of CO_2 and NaOH . This includes ice, NaOH with various numbers of hydrate water, Na_2CO_3 with various numbers of hydrate water, NaHCO_3 , and the salts Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and Wegscheiderite ($3\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3$). The equilibrium between an aqueous phase and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(s)$ is described by the equation:



The equilibrium in equation (7.6) can be expressed mathematically using the fact that at equilibrium, the chemical potential of the salt is equal to the chemical potentials of the salts constituent parts. The chemical potentials are written as in equation (4.6) and (4.8) and this equilibrium condition can be written as:

$$-\frac{2\mu_{\text{Na}^+(aq)}^* + \mu_{\text{CO}_3^{2-}(aq)}^* + 10\mu_{\text{H}_2\text{O}(l)}^0 - \mu_{\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(s)}^0}{RT} = \ln \left(\left(a_{\text{Na}^+(aq)}^* \right)^2 a_{\text{CO}_3^{2-}(aq)}^* a_{\text{H}_2\text{O}(l)}^{10} \right) \quad (7.7)$$

In order for thermodynamic models to be able to accurately predict the solubility of salts like $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(s)$, it is required that the model calculates the water activity very accurately. As it appears from equation (7.7), the water activity raised to the tenth power is part of this equation. A small inaccuracy in the water activity will therefore give a large error in the calculated solubility of the salt.

65 Wagman D.D., Evans W.H., Parker V.B., Schumm R.H., Halow I., Bailey S.M., Churney K.L., and Nuttall R.L., "The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C₁ and C₂ organic substances in SI units", J. Phys. Chem. Ref. Data 11(1982), Suppl. 2

For the solid salt, the state of pure, crystalline salt is used as standard state. Salts precipitating from aqueous solutions are usually pure, crystalline salts. In some cases solid solutions precipitate from a solution. This is for example the case for many solutions of potassium and ammonium salts. The potassium and the ammonium ions are of similar size and can therefore replace each other in the crystal lattices of their salts.

As mentioned above, in an aqueous solution of CO₂ and NaOH, many solid phases can form. After a speciation equilibrium calculation is performed the degree of saturation of these various solid phases can be calculated. The degree of saturation can be determined by using the saturation index.

7.2.1 Saturation index

The degree of saturation or the saturation index, SI, of a salt is defined as the activity product of a salt divided by its solubility product. For the salt in equation (7.7):

$$SI = \frac{\left(a_{Na^+(aq)}^*\right)^2 a_{CO_3^{2-}(aq)}^* a_{H_2O(l)}^{10}}{K_{Na_2CO_3 \cdot 10H_2O(s)}} \quad (7.8)$$

The solubility product K is defined by equation (7.5). The saturation index of a salt is unity at saturation. In a supersaturated solution it is greater than one and in unsaturated solutions it is less than one. The saturation index of a salt indicates if the salt possibly will precipitate. Often a number of salts are simultaneously supersaturated in a solution.

The first precipitation of salt will be determined by crystallization kinetics. When the solution eventually has reached equilibrium, some of the salts first formed might have dissolved again.

7.3 Vapor-liquid equilibrium

At equilibrium between CO₂ in the aqueous phase and CO₂ in the gas phase at the temperature T and the pressure P , the chemical potential of CO₂ must be identical in the two phases:

$$CO_2(g) \rightleftharpoons CO_2(aq) \quad (7.9)$$

$$\mu_{CO_2(g)} = \mu_{CO_2(aq)}$$

The chemical potential of CO₂ in the gas phase at T and P can be expressed by the fugacity coefficient $\hat{\phi}_{CO_2(g)}$ of CO₂ in the gas phase according to equation (6.78):

$$\mu_{CO_2(g)}(T, P) = \mu_{CO_2}^{0,ig}(T, P_0) + RT \ln \frac{y_{CO_2(g)} P \hat{\phi}_{CO_2(g)}}{P_0} \quad (7.10)$$

The mole fraction of CO₂ in the gas phase is represented by y . The chemical potential of CO₂ in the aqueous phase can be expressed by equation (6.79):

$$\mu_{CO_2(aq)}(T, P) = \mu_{CO_2(aq)}^* + V_{CO_2(aq)}(P - P_0) + RT \ln \left(x_{CO_2(aq)} \gamma_{CO_2(aq)}^* \right) \quad (7.11)$$

The condition for vapor-liquid equilibrium can be formulated by combining equations (7.10) and (7.11):

$$\frac{\mu_{CO_2(aq)}^* - \mu_{CO_2}^{0,ig}(T, P_0)}{RT} + \frac{V_{CO_2(aq)}(P - P_0)}{RT} = \ln \left(\frac{y_{CO_2} \hat{\phi}_{CO_2} P}{x_{CO_2} \gamma_{CO_2}^* P_0} \right) \quad (7.12)$$

At low pressures and high temperatures, the fugacity coefficient is very close to 1 and can be ignored. Also the pressure correction to the aqueous phase chemical potential is often ignored at low pressures. For calculation at high pressure, the activity coefficient model can be combined with an equation of state for calculating the fugacity coefficients [47]. The partial molar volume of the volatile component in the aqueous phase is often replaced with the standard state molar volume. This method of performing vapor-liquid equilibrium calculations is often called the “gamma/phi formulation of VLE”.

7.3.1 Henry's constant

Henry's constant is often used in vapor-liquid equilibrium calculations with electrolyte solutions. Henry's constant $H(T, P)$ is defined as [2]:

$$\lim_{x_i \rightarrow 0} \frac{y_i \hat{\phi}_i P}{x_i} = H_i(T, P) \quad (7.13)$$

Henry's constant has therefore same unit as pressure. Alternatively, Henry's constant can be defined based on molality. Then the molality m_i replaces the mole fraction x_i in equation (7.13) and the unit of this Henry's constant is (pressure unit · kg H₂O)/mol.

Henry's constant is often used for vapor-liquid equilibrium calculations for sparingly soluble gases according to the definition in equation (7.13).

The pressure dependence of Henry's constant is [2]:

$$H_i(T, P) = H_i(T, P_0) \cdot \exp\left(\frac{V_{i(aq)}^* (P - P_0)}{RT}\right) \quad (7.14)$$

By writing equation (7.12) for the general case of gas i and letting x_i go towards zero, the definition of Henry's constant, equation (7.13) can be inserted and the following is obtained as γ_i^* goes towards unity for x_i going towards zero:

$$\frac{\mu_{i(aq)}^* - \mu_i^{0,ig}(T, P_0)}{RT} + \frac{V_{i(aq)}^* (P - P_0)}{RT} = \ln\left(\frac{H_i(T, P)}{P_0}\right) \quad (7.15)$$

$V_{i(aq)}^*$ is the standard state partial molar volume of species i in the aqueous phase defined in equation (5.41). P_0 is the pressure at which the chemical potential of component i as ideal gas is known.

By combining equations (7.14) and (7.15) the following relation is obtained:

$$\frac{\mu_{i(aq)}^* - \mu_i^{0,ig}(T, P_0)}{RT} = \ln\left(\frac{H_i(T, P_0)}{P_0}\right) \quad (7.16)$$

Henry's constant can thus be used for calculating standard state properties of a volatile component. If the chemical potential $\mu_i^{0,ig}$ of the volatile component in the gas phase is known, the chemical potential of the component in the aqueous phase $\mu_{i,aq}^*$ can be calculated from (7.16) and vice versa.

Henry's constant can also be used for vapor-liquid equilibrium at super-critical conditions where pure component standard state properties are not available. By inserting equation (7.16) in equation (7.12) the following is obtained:

$$\ln\left(\frac{H_i(T, P_0)}{P_0}\right) + \frac{V_i(P - P_0)}{RT} = \ln\left(\frac{y_i \hat{\phi}_i P}{x_i \gamma_i^* P_0}\right) \quad (7.17)$$

At pressures above the boiling point pressure of the solvent, an empirical form of the equation is often used:

$$\ln\left(\frac{H_i(T, P_{w, sat})}{P_0}\right) + \frac{V_i^*(P - P_{w, sat})}{RT} = \ln\left(\frac{y_i \hat{\phi}_i P}{x_i \gamma_i^* P_0}\right) \quad (7.18)$$

This equation is known as the Krichevski-Iliinskaya equation [66]. In this equation, P_0 is 1 bar, $P_{w, sat}$ is the vapor pressure of the solvent at the relevant temperature and P is the total pressure. In this empirical form of the equation, the standard state volume of the solute is used rather than the partial molar volume of the solute.

Exercise 7.1

Natural gas is transported in an off-shore pipeline. Natural gas contains CO_2 and H_2O besides light alkanes. During the transport, the pipe is cooled by the surrounding ocean water. Part of the water from the gas phase is condensing to form a liquid phase. CO_2 is dissolving in the liquid phase, creating an acidic, corrosive mixture. A sodium hydroxide solution is added to the gas stream in order to prevent corrosion. After the transport, a sample was taken out. It contained approximately 1 mol of $\text{Na}^+(\text{aq})$ per kg water and 1.5 mol of dissolved CO_2 per kg water.

Perform a speciation equilibrium calculation at 25 °C to determine the amount of each of the components. Assume that the molal activity coefficients for solutes and the mole fraction activity coefficient of water are equal to 1. Use data from Table 7.1 to determine the equilibrium constants. Calculate the pH of the solution, still assuming molal activity coefficients of solutes equal to 1. pH is defined as:

$$\text{pH} = -\log_{10} a_{\text{H}^+}^m$$

Calculate the partial pressure of CO_2 in equilibrium with the solution, assuming that fugacity coefficients are equal to 1.

Table 7.1: Standard state Gibbs energies of some ions, CO_2 and H_2O . The molal standard state (aq) is used for solutes, the pure component standard state is used for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$.

Component	$\text{CO}_2(\text{g})$	$\text{CO}_2(\text{aq})$	$\text{HCO}_3^-(\text{aq})$	$\text{CO}_3^{2-}(\text{aq})$	$\text{H}_2\text{O}(\text{l})$	$\text{H}^+(\text{aq})$	$\text{OH}^-(\text{aq})$
$\Delta_f G$, kJ/mol	-394.359	-385.980	-586.77	-527.81	-237.129	0.0	-157.248

7.4 Liquid-Liquid equilibrium

When equilibrium is established between two liquid phases, the activity of each independent component is the same in both phases. For a system of NaCl, water and isopropanol (IP) three equations can be written for the equilibrium of the three independent components between liquid phase I and liquid phase II:

66 Krichevsky I and Iliinskaya A, Partial molal volumes of gases dissolved in liquids (a contribution to the thermodynamics of dilute solutions of non-electrolytes), Acta Physico-chim URSS, 20(1945)327-348

$$\begin{aligned}
\mu_{NaCl}^* + \nu RT \ln a_{\pm}^{*,I} &= \mu_{NaCl}^* + \nu RT \ln a_{\pm}^{*,II} \\
\mu_{H_2O}^0 + RT \ln a_{H_2O}^I &= \mu_{H_2O}^0 + RT \ln a_{H_2O}^I \\
\mu_{IP}^* + RT \ln a_{IP}^{*,I} &= \mu_{IP}^* + RT \ln a_{IP}^{*,I}
\end{aligned}
\tag{7.19}$$

The standard state chemical potentials cancel each other and the three equations can be reduced to:

$$\begin{aligned}
0 &= a_{\pm}^{*,II} - a_{\pm}^{*,I} \\
0 &= a_{H_2O}^{II} - a_{H_2O}^I \\
0 &= a_{IP}^{II} - a_{IP}^I
\end{aligned}
\tag{7.20}$$

In equation (7.19) the chemical potential of the salt defined as $\mu_{NaCl} = \nu_{Na^+} \mu_{Na^+} + \nu_{Cl^-} \mu_{Cl^-}$ is used rather than the chemical potentials of the individual ions. Each of the two phases need to be electrically neutral. The passage of one cation from phase *I* to phase *II* must be followed by another cation passing the opposite way or an anion passing the same way. Therefore it is the chemical potential of the salts that should be considered and not those of the individual ions.

For solutions containing more salts, an additional equation for the mean activity of each independent salt has to be used.

If a liquid-liquid equilibrium system instead was modeled as a pseudo binary system with a mixed solvent and one or more salts, the standard state chemical potentials of the salts would have been different in the two phases. The system of equations to be solved in the equilibrium calculation would then be far more complicated than equation (7.20).

7.5 Composition dependence of equilibrium constants

The standard state of the ions was chosen as the pure component standard state of solutes in water normalized so that the activity coefficient of an ion has the value one at infinite dilution in water. Therefore equation (7.7) can be applied to solid-liquid equilibria occurring in mixed solvent solutions too. The standard state chemical potentials on the left hand side of equation (7.7) are unchanged by the fact that an organic solvent is present. The equilibrium constants are therefore independent of the composition.

The relative permittivity ϵ_r is much lower in organic solvents than in water. Variations of the relative permittivity of aqueous solutions with the concentration of ethanol and of sodium chloride are shown in Figure 7.1.

Because of the different dielectric properties, the electromotive force measured for a reaction in water is much higher than for the same measurements performed in a mixture of water and organic solvents. The standard potentials (E^0) determined in such mixtures are also different

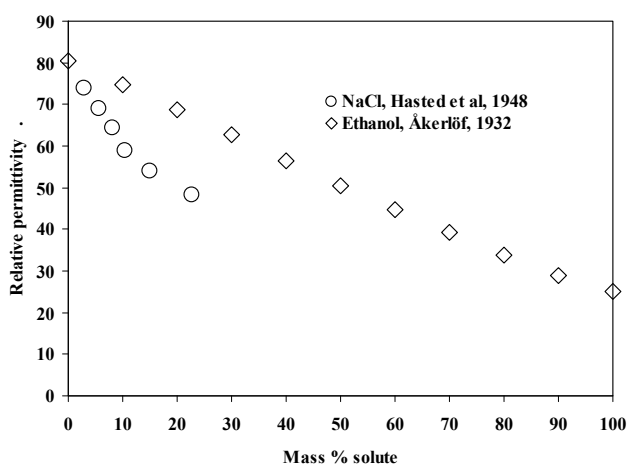


Figure 7.1: The relative permittivity of aqueous solutions of ethanol and of NaCl

from those measured in water. Hence the standard state chemical potentials of ions in this mixed solvent solution are different from those in water.

The difference between the standard state chemical potential of an ion in two solvents with different relative permittivities can be evaluated analytically using the Born equation (6.26) under the assumption that the difference in Helmholtz energy is identical to the difference in Gibbs energy.

The standard state chemical potentials of solutes are different in a “mixed solvent” from the corresponding values in water. If the ideal solution is defined as in equation (3.1), the values of the standard state chemical potentials are defined as the standard state chemical potentials of solutes in pure water. Any deviation from ideal solution behavior is handled by the activity coefficients. There is no reason to switch to other standard state chemical potentials.

By choosing the standard state for solutes as that of pure solutes, normalized so that the activity coefficients are one at infinite dilution in water and the standard state for water as the pure component standard state, the definition of the ideal solution is established. The ionic and molecular interactions are determined on the basis of this definition of the ideal solution and the corresponding excess Gibbs energy function. This method of describing the thermodynamic properties of mixed solvent electrolyte solutions was first presented by Thomsen and Rasmussen [47] for water-ammonia-salt systems. It was later expanded by Iliuta et al. [49] to salt systems with methanol and by Thomsen et al. [50] to salt systems with ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, sec-butanol and tert-butanol.

In Figure 7.2 an example of a liquid-liquid equilibrium calculation in the NaCl – n-butanol – H₂O system at 40 °C is shown. There is a very good agreement between the experimental and calculated equilibrium compositions. In Figure 7.3 an example of vapor-liquid equilibrium in the NaCl – ethanol – H₂O system is shown. The effect of adding sodium chloride to an ethanol-water mixture is that the partial pressure of ethanol is increased. Sodium chloride thus has a salting out effect on ethanol. The effect is highest in the solutions containing most water. The solubility of NaCl in solutions with high ethanol content is quite low. Therefore sodium chloride does not have a significant effect on such solutions. The ethanol – water system forms an azeotrope at 96% ethanol by mass. The solubility of NaCl in the azeotropic solution is too low to have a significant effect on the azeotrope. In Figure 7.4 the solubility of KNO₃ in water-ethanol mixtures is shown together with experimental data at various temperatures from 15 to 75 °C. The solubility of KNO₃ in pure ethanol is seen to be much lower than the solubility in water, especially at low temperatures.

The calculation results in Figure 7.2 and Figure 7.4 were only possible because the standard states were chosen so that the equilibrium constants were independent of composition. The vapor-liquid equilibrium calculation in Figure 7.3 is different because it only requires that the standard state chemical potentials of the pure solvent components are known. It has only been possible to perform the three types of calculations presented in Figure 7.2, Figure 7.3, and Figure 7.4 using the same parameter set for all the calculations with the Extended UNIQUAC model using standard state properties independent of solvent composition [49, 50]. Similar results have not been published using other models.

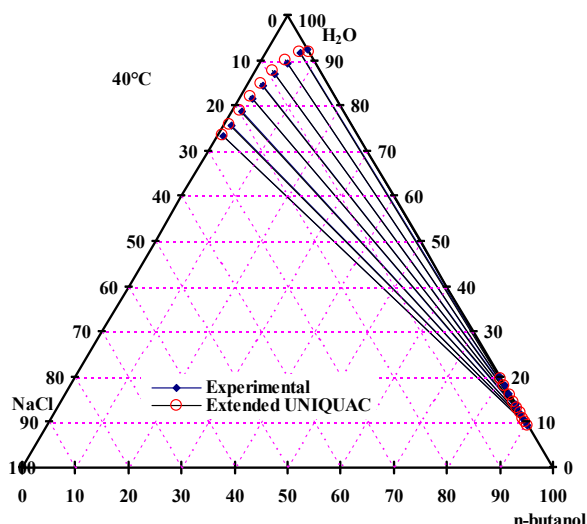


Figure 7.2: Experimental liquid-liquid equilibrium data in the NaCl - n-butanol - H₂O system at 40 °C and corresponding values calculated with the Extended UNIQUAC model

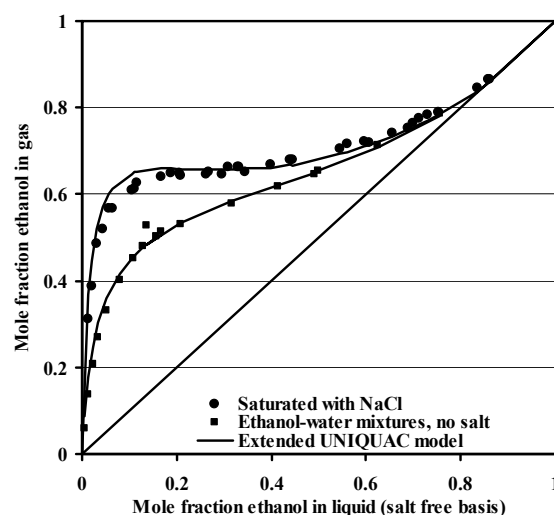


Figure 7.3: Vapor-liquid equilibrium in the ethanol-water-NaCl systems at 1 bar. Experimental data and data calculated with Extended UNIQUAC model

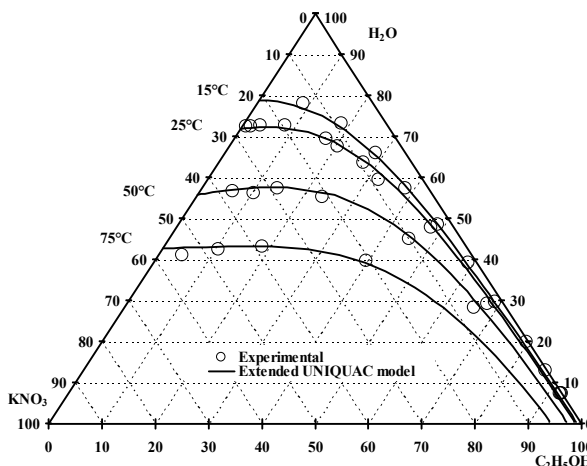


Figure 7.4: The solubility of KNO₃ in the ethanol-water system at temperatures from 15 to 75 °C. Experimental data and data calculated with Extended UNIQUAC model

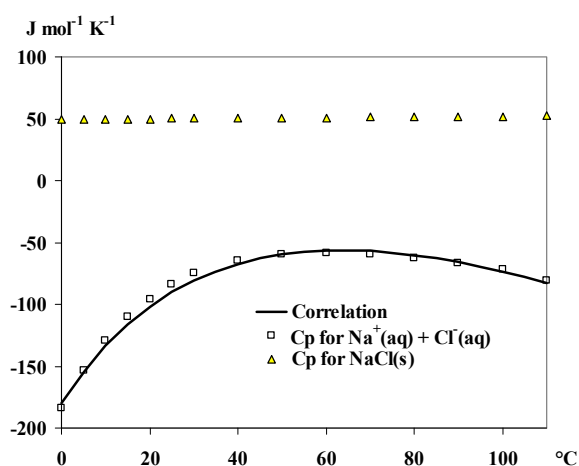


Figure 7.5: The standard state heat capacity for solid NaCl and for aqueous NaCl as a function of temperature

The standard state for solutes could have been chosen as for example the pure solutes, normalized so that the activity coefficients were one at infinite dilution in a solution consisting of 50 % ethanol in water. The standard state for the solvents could be the pure solvent components. If that was the case, a new ideal solution would in fact have been defined. A really serious problem with that method is that it seems like a new definition of the ideal solution and consequently a new excess Gibbs function is required for each solvent composition.

Based on the definition of the ideal solution in section 3.1 and the definition of the excess term in section 4.2, the chemical potential of component i is written:

$$\mu_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_i^* \quad (7.21)$$

The activity coefficient is dependent of composition but the standard state chemical potential is not. All deviation from ideality is handled by the excess term of the chemical potential.

In the “Mixed solvent approach”, the standard state chemical potentials are functions of composition. The chemical potential of component i according to this approach is written:

$$\mu_i = \mu_i^{MS}(x) + RT \ln x_i + RT \ln \gamma_i^{MS} \quad (7.22)$$

MS indicates the mixed solvent approach. In this approach, the standard state chemical potential is a function of composition, which is indicated by the (x) . The excess term is also a function of composition.

Considering a water – organic solvent mixture to be a pseudo solvent that should be modeled separately with its own standard state chemical potentials for solutes adds unnecessary complexity to the problem and has only been successful for limited systems [67, 68].

7.6 Temperature dependence of equilibrium constants

There are various ways of calculating the equilibrium constants necessary for performing equilibrium calculations. In some applications, the equilibrium constants are given as empirical functions of temperature. The approach suggested in these notes is to calculate the equilibrium constants from standard state chemical potentials. This is the method used in connection with the Extended UNIQUAC model.

Values for the standard state chemical potentials for solutes, solids, and gases can be found tabulated for 298.15 K and 1 bar [3, 65]. The value of ΔG^0 at the temperature of interest has to be calculated from its value at 298.15 K. This can be done by using the Gibbs-Helmholtz equation:

$$-\frac{d \ln K}{dT} = \frac{d(\Delta G^0 / (RT))}{dT} = -\frac{\Delta H^0}{RT^2} \text{ at constant pressure} \quad (7.23)$$

By integrating this equation from the standard state temperature $T_0 = 298.15$ K to the temperature T , one obtains

$$\ln K_T - \ln K_{T_0} = \int_{T_0}^T \frac{\Delta H^0}{RT^2} dT \quad (7.24)$$

The variation of ΔH^0 , the change in standard state enthalpy by the process, with temperature, can be calculated from the heat capacity of the species involved in the process.

$$\frac{d\Delta H^0}{dT} = \Delta C_p^0 \quad (7.25)$$

ΔC_p^0 is the increment in standard state heat capacity by the reaction considered. The standard state heat capacities of pure crystalline salts are often nearly constant in the temperature range from 0 to 110°C. For ions however, the standard state heat capacity rises steeply between 0 and 25°C, less steeply up to about 50°C and then decreases slightly. This is illustrated in Figure 7.5, which is based on data for NaCl correlated by Clarke and Glew [69]. The standard state heat capacity for aqueous NaCl is the sum of the standard state heat capacities for $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$. Obviously ΔC_p^0 can not be considered temperature independent. A

67 Lorimer, JW, “Thermodynamics of solubility in mixed solvent systems”, Pure & Appl. Chem., 65(1993) 183-191

68 Kamps AP-S, “Model for the Gibbs Excess Energy of Mixed-Solvent (Chemical-Reacting and Gas-containing) Electrolyte Systems, Ind. & Eng. Chem. Res., 44(2005)201-225

69 Clarke E.C.W., and Glew D.N., “Evaluation of the Thermodynamic Functions for Aqueous Sodium Chloride from Equilibrium and Calorimetric Measurements below 154°C”, J. Phys. Chem. Ref. Data, 14(1985) 489-610.

correlation for $C_{p,i}^*$, the standard state heat capacity for ion i , of the form:

$$C_{p,i}^* = a_i + b_i T + \frac{c_i}{T - T_{\Theta,i}} \quad (7.26)$$

was suggested by Helgeson *et al.* [70]. The term $T - T_{\Theta,i}$ provides for the steep change in $C_{p,i}^*$ below 25°C. This correlation is used with the Extended UNIQUAC model. $T_{\Theta,i}$ is given the constant value 200 K for all components., and the a_i , b_i , and c_i parameters are fitted to experimental heat capacity data rather than calculated as suggested by Helgeson *et al.*. The performance of this correlation is illustrated for aqueous NaCl in Figure 7.5.

The expression (7.26) for the standard state heat capacity can be used for water, ions and crystalline salts. For crystalline salts the b and the c parameters are set to zero, assuming that the heat capacities of all crystalline salts behave similar to that of NaCl (Figure 7.5). ΔC_p^0 can then be expressed in terms of Δa , Δb , and Δc , the increments in the a , b , and c parameters by the process. Integration of equation (7.25) gives:

$$\Delta H_T^0 = \Delta H_{T_0}^0 + \Delta a(T - T_0) + 0.5\Delta b(T^2 - T_0^2) + \Delta c \ln \frac{T - T_{\Theta}}{T_0 - T_{\Theta}} \quad (7.27)$$

In this equation, ΔH_T^0 is the increment in standard state enthalpy at the temperature T . By inserting this expression in equation (7.24) and integrating, one obtains:

$$\begin{aligned} R \ln K_T = R \ln K_{T_0} - \Delta H_{T_0}^0 \left(\frac{1}{T} - \frac{1}{T_0} \right) + \Delta a \left(\ln \frac{T}{T_0} + \frac{T_0}{T} - 1 \right) \\ + 0.5\Delta b \left(\frac{(T - T_0)^2}{T} \right) + \frac{\Delta c}{T_{\Theta}} \left(\frac{T - T_{\Theta}}{T} \ln \frac{T - T_{\Theta}}{T_0 - T_{\Theta}} - \ln \frac{T}{T_0} \right) \end{aligned} \quad (7.28)$$

With this value of the equilibrium constant, the composition of the solution can be calculated at the temperature T if the activity coefficients are known at this temperature.

7.7 Pressure dependence of equilibrium constants

Solid liquid equilibria are influenced by pressure due to the difference in the partial molar volume of the salt and of its constituent parts. This is especially important in connection with oil production and the production of geothermal energy. Brines are being pumped from reservoirs with high temperature and pressure to areas with lower temperature and pressure. Sulfates and carbonates of calcium, strontium, and barium are examples of salts whose solubility decrease with decreasing pressure.

The pressure dependence of the standard state chemical potential was given in equation (5.41):

$$\left[\frac{\partial \mu_i}{\partial P} \right]_T = V_i \quad (7.29)$$

It follows that:

70 Helgeson H.C., Kirkham D.H., and Flowers G.C., "Theoretical Prediction of the Thermodynamic Behaviour of Aqueous Electrolytes at High Pressures and Temperatures IV", American Journal of Science, 281(1981) 1249-1516.

$$\left(\frac{\partial \ln K}{\partial P} \right)_T = -\frac{\Delta_{dis} V}{RT} \quad (7.30)$$

$\Delta_{dis} V$ is the increment in standard state volume by the dissolution process. For the dissolution of $BaSO_4$ in water, the process is:



The increment in standard state volume by this process is:

$$\Delta_{dis} V = V_{Ba^{2+}(aq)} + V_{SO_4^{2-}(aq)} - V_{BaSO_4(s)} \quad (7.32)$$

The standard state volumes changes a little by pressure and so does the increment in standard state volume. In order to integrate equation (7.30) the pressure dependence of the increment in standard state volume therefore has to be considered. This pressure dependence is expressed by:

$$\left(\frac{\partial \Delta_{dis} V}{\partial P} \right)_T = -\Delta_{dis} \kappa \quad (7.33)$$

Here, $\Delta_{dis} \kappa$ is the increment in standard partial molar compressibility for the same dissolution process. This compressibility increment is considered pressure independent here. According to Lown *et al.* [71], the molar compressibility for different acid-base equilibria could be assumed pressure independent in the range 1-2000 bar. Equation (7.33) can therefore be integrated from the pressure P_0 at which the standard state chemical potentials are known to the desired pressure P to give at constant temperature:

$$\Delta_{dis} V_P - \Delta_{dis} V_{P_0} = -\Delta_{dis} \kappa (P - P_0)$$

This result is inserted into equation (7.30) which is then integrated to give:

$$\ln K_P = \ln K_{P_0} - \frac{\Delta_{dis} V_{P_0}}{RT} (P - P_0) + \frac{\Delta_{dis} \kappa}{2RT} (P - P_0)^2 \quad (7.34)$$

Usually the increment in standard molar volume and in standard molar compressibility is not known with enough accuracy to determine the pressure dependence of equilibrium constants. These two values can instead be considered as adjustable parameters for each salt and be fitted to equation (7.34).

Activity coefficient models do not give the pressure dependence of the activity coefficients. It was shown by García *et al.* [52] that the total influence of pressure on solid-liquid equilibrium can be accounted for by introducing another equation similar to equation (7.34) for the activity coefficients.

7.7.1 The pressure dependence of activity coefficients

From the definition of $RT \ln \gamma_i$ as the excess contribution to the chemical potential, it follows that the pressure dependence of $RT \ln \gamma_i$ corresponds to the pressure dependence of the chemical potential:

$$\left(\frac{\partial \ln \gamma_i^*}{\partial P} \right)_{T,n} = \frac{V_i^{ex}}{RT} \quad (7.35)$$

71 Lown, D.A., Thirsk, H.R., Lord W.J., "Effect of pressure on ionization equilibria in water at 25°C", *Trans. Faraday Soc.* 64(1968)2073-2080.

It follows that the activity coefficients at the pressure P can be calculated from the activity coefficients at the pressure P_0 by an equation similar to (7.34)

$$\ln \gamma_{i,P}^* = \ln \gamma_{i,P_0}^* + \frac{V_{i,P_0}^{ex}}{RT} (P - P_0) - \frac{\kappa_i^{ex}}{2RT} (P - P_0)^2 \quad (7.36)$$

V_{i,P_0}^{ex} is the partial molar excess volume of component i at the pressure P_0 , and κ_i^{ex} is the excess molar compressibility of component i . The equation for solid-liquid equilibrium at the pressure P can now be written according to the general equation (7.5):

$$\ln K_P = \sum \nu_i \ln (x_i \gamma_i(T, P)) \quad (7.37)$$

No superscript is being used for the activity coefficient as the term covers both water and solutes.

By use of equation (7.34) and (7.36), equation (7.37) can be expanded to:

$$\begin{aligned} \ln K_{P_0} - \frac{\Delta_{dis} V_{P_0}}{RT} (P - P_0) + \frac{\Delta_{dis} \kappa}{2RT} (P - P_0)^2 \\ = \sum_i \nu_i \left(\ln x_i + \ln \gamma_{i,P_0} + \frac{V_{i,P_0}^{ex}}{RT} (P - P_0) - \frac{\kappa_i^{ex}}{2RT} (P - P_0)^2 \right) \end{aligned} \quad (7.38)$$

Pressure terms are collected on the left hand side of the equation together with $\ln K_{P_0}$:

$$\begin{aligned} \ln K_{P_0} - \left(\frac{\Delta_{dis} V_{P_0}}{RT} + \sum_i \nu_i \frac{V_{i,P_0}^{ex}}{RT} \right) (P - P_0) + \left(\frac{\Delta_{dis} \kappa}{2RT} + \sum_i \nu_i \frac{\kappa_i^{ex}}{2RT} \right) (P - P_0)^2 \\ = \sum_i \nu_i \ln (x_i \gamma_{i,P_0}) \end{aligned} \quad (7.39)$$

The coefficients to $P - P_0$ and $(P - P_0)^2$ have physical meaning, but are not known with enough accuracy to be used for equilibrium calculations. They are given the symbols α and β and are treated as adjustable parameters, independent of temperature. The equilibrium equation is then reduced to:

$$\ln K_{P_0} + \alpha (P - P_0) + \beta (P - P_0)^2 = \sum_i \nu_i \ln (x_i \gamma_{i,P_0}) \quad (7.40)$$

This simple equation works very well for solid-liquid equilibrium under high pressure, as shown by Garcia *et al.* [52,53]. The pressure parameters determined by A.V. Garcia are given in Table 7.2.

Table 7.2: Pressure parameters determined by A.V. Garcia for common scaling minerals.

Salt	α , bar ⁻¹	β , bar ⁻²	Salt	α , bar ⁻¹	β , bar ⁻²
BaSO ₄	1.636629×10 ⁻³	3.333826×10 ⁻⁷	CaSO ₄ ·2H ₂ O	1.078224×10 ⁻³	3.078141×10 ⁻⁷
SrSO ₄	1.035686×10 ⁻³	7.153236×10 ⁻⁷	NaCl	9.927134×10 ⁻⁵	-1.358719×10 ⁻⁸
CaSO ₄	2.328718×10 ⁻³	-8.421355×10 ⁻⁷	CaCO ₃	-3.916945×10 ⁻³	-2.092925×10 ⁻⁵

8 Thermal and volumetric properties

8.1 Partial and apparent molar properties

A partial molar property is defined as the partial molar derivative of the property. For the property M , the partial molar property of component i is defined as:

$$M_i \equiv \left[\frac{\partial (nM)}{\partial n_i} \right]_{P,T,n_j} \quad (8.1)$$

It can be shown that

$$nM = \sum_i n_i M_i \quad (8.2)$$

For electrolytes, it has been found practical to use apparent molar properties in addition to partial molar properties. An apparent molar property of the molar property M is often indicated with the greek letter *phi* (M_ϕ or Φ_M). Apparent molar properties are only used to describe the properties of binary solutions, usually it is therefore not indicated which component the property applies to.

The apparent molar property of the salt S in an aqueous solution is defined by an equation similar to (8.2):

$$nM = n_w M_w^0 + n_s M_\phi$$

$$M_\phi \equiv \frac{nM - n_w M_w^0}{n_s} \quad (8.3)$$

In this equation, M_w^0 is the molar property of pure water. When calculating the apparent molar property of a salt, the solvent is considered ideal, and all deviation from ideality is assigned to the salt. The apparent molar property of the solvent is calculated by considering the salt ideal and assigning all deviation from ideality to the solvent.

The property M can be written as a sum of the contribution from standard state properties and the contribution from excess properties:

$$nM = n_s M_s^* + n_s M_s^{ex} + n_w M_w^0 + n_w M_w^{ex} \quad (8.4)$$

By inserting this expression into the definition of the apparent molar property, it can be written as:

$$M_\phi = \frac{n_s M_s^* + n_s M_s^{ex} + n_w M_w^0 + n_w M_w^{ex} - n_w M_w^0}{n_s} = M_s^* + \frac{n_s M_s^{ex} + n_w M_w^{ex}}{n_s} \quad (8.5)$$

From this expression it is clear that the apparent property is equal to the standard state property plus the total excess contribution per mole salt. Equation (8.5) also shows that in the ideal solution, the apparent molar property is identical to the standard state property, because the excess contribution is zero in the ideal solution.

8.2 Thermal properties

The chemical potential of a solvent component is:

$$\mu_i = \mu_i^0 + RT \ln(x_i \gamma_i) \quad (8.6)$$

By differentiation of equation (8.6), applied to water, with respect to temperature at constant

pressure and composition one obtains

$$\left[\frac{\partial \left(\frac{\mu_w}{RT} \right)}{\partial T} \right]_{P,x} = \left[\frac{\partial \left(\frac{\mu_w^0}{RT} \right)}{\partial T} \right]_{P,x} + \left[\frac{\partial \ln \gamma_w}{\partial T} \right]_{P,x} \quad (8.7)$$

$$\frac{H_w}{RT^2} = \frac{H_w^0}{RT^2} + \frac{H_w^{ex}}{RT^2}$$

H_w is the partial molar enthalpy, H_w^0 is the molar enthalpy of formation in the standard state, and H_w^{ex} is the partial molar excess enthalpy of water. The composition of electrolyte solutions, which are not fully dissociated, is dependent on temperature because the equilibrium constants are dependent on temperature as discussed in section 7.6. The reactions involved in speciation usually have a significant enthalpy effect. Equation (8.7) is therefore only valid in the special case, where speciation can be ignored.

The chemical potential of an ion is:

$$\mu_i = \mu_i^* + RT \ln(x_i \gamma_i^*) \quad (8.8)$$

Differentiation with respect to temperature of equation (8.8) at constant pressure and composition yields:

$$\left[\frac{\partial \left(\frac{\mu_i}{RT} \right)}{\partial T} \right]_{P,x} = \left[\frac{\partial \left(\frac{\mu_i^*}{RT} \right)}{\partial T} \right]_{P,x} + \left[\frac{\partial \ln \gamma_i^*}{\partial T} \right]_{P,x} \quad (8.9)$$

$$\frac{H_i}{RT^2} = \frac{H_i^*}{RT^2} + \frac{H_i^{ex}}{RT^2}$$

H_i is the partial molar enthalpy, H_i^* is the standard state enthalpy of formation, and H_i^{ex} is the partial molar excess enthalpy of ion i .

The standard state enthalpy of a solute is the same in the unsymmetrical mole fraction system and the molal system. This is because the difference between the two standard state chemical potentials divided by RT is independent of temperature according to equation (4.12):

$$\frac{\mu_i^* - \mu_i^m}{RT} = -\ln(M_w m_0) \quad (8.10)$$

Using the results from equations (8.7) and (8.9), the total enthalpy of formation of an electrolyte solution is calculated at constant pressure and composition as:

$$nH_x = \tilde{n}_w (H_w^0 + H_w^{ex}) + \sum_i \tilde{n}_i (H_i^* + H_i^{ex}) \quad (8.11)$$

The composition at which the enthalpy in equation (8.11) is calculated is the equilibrium composition achieved after speciation equilibrium is established. The amount of ions and water used in equation (8.11) is therefore not necessarily equal to the amount of ions and water mixed to form the solution. Therefore these amounts are marked with tilde (\sim). From equation (8.11), the partial molar enthalpies of water H_w and of salt H_s can be evaluated by numerical differentiation at constant temperature:

$$H_w = \left[\frac{\Delta(nH_x)}{\Delta n_w} \right]_{P,T,n=Eq} \quad (8.12)$$

$$L_w \equiv H_w - H_w^0$$

The subscript $n = Eq$ signifies that mol of salt is constant but the enthalpy is calculated at the equilibrium composition (after speciation). L_w is the partial relative molar enthalpy of water defined as the partial molar enthalpy of water minus the standard state enthalpy of formation of water, H_w^0 . The partial relative enthalpy of water consists of the molar excess enthalpy of water plus the enthalpy changes occurring from speciation in the solution by adding one mol of water.

The partial molar enthalpy H_s of salt and the partial relative molar enthalpy of salt L_s are similarly given by:

$$H_s = \left[\frac{\Delta(nH_x)}{\Delta n_s} \right]_{P,T,n=Eq} \quad (8.13)$$

$$L_s \equiv H_s - \sum_i \nu_i H_i^*$$

The stoichiometric coefficient ν_i indicates that the summation only includes the ions of the salt for which the partial molar enthalpy is calculated, not for the ions formed by speciation. The enthalpy changes caused by speciation in the solution are now included in L_w and L_s . The relative enthalpy of a solution is:

$$nL = n_w L_w + n_s L_s \quad (8.14)$$

It follows from equation (8.12), (8.13), and (8.14) that *the relative enthalpy of a solution of water and salt is identical to the enthalpy of formation of the solution minus the aqueous standard state enthalpy of formation of the quantity of water and salts used for forming the solution.*

The apparent relative molar enthalpy L_ϕ of the salt can be written according to the definition of an apparent molar property:

$$L_\phi = \frac{n_w L_w + n_s L_s - n_w L_w^0}{n_s} = \frac{nL}{n_s} \quad (8.15)$$

The term L_w^0 for pure water is considered to be zero because there is no speciation except the autoprotolysis of water and there is no excess enthalpy for pure water. The amount of water, n_w and the amount of salt, n_s used in equation (8.15) are the original amounts of water and salt mixed to form a solution.

The temperature derivative of L_ϕ is the relative molar heat capacity J . L is determined from equation (8.15) and differentiated with respect to temperature at constant pressure:

$$nJ = \left[\frac{\partial(n_s L_\phi)}{\partial T} \right]_{P,n=Eq} \quad (8.16)$$

By inserting the expressions for $n_w L_w$ and $n_s L_\phi$, from equations (8.12) and (8.13) the heat capacity can be determined as:

$$nJ = \left[\frac{\partial (n_S L_\phi)}{\partial T} \right]_{P,n=Eq} = \frac{\partial (n_w H_w)}{\partial T} - \frac{\partial (n_w H_w^0)}{\partial T} + \frac{\partial (n_S H_S)}{\partial T} - n_S \sum_{ions} \nu_i \frac{\partial (n_i H_i^*)}{\partial T}$$

$$= n_w C_{p,w} - n_w C_{p,w}^0 + n_S C_{p,S} - n_S \sum_{ions} \nu_i C_{p,i}^* = n_S \left(C_{p,\phi} - \sum_{ions} \nu_i C_{p,i}^* \right)$$

$C_{p,i}^*$ is the standard state molar heat capacity of ion i . $C_{p,\phi}$ is the apparent molar heat capacity of the salt:

$$C_{p,\phi} = \frac{n_w C_{p,w} + n_S C_{p,S} - n_w C_{p,w}^0}{n_S}$$

From equations (8.15) and (8.17) it can be seen that the relative molar enthalpy and the relative molar heat capacity are equal to zero in the ideal solution only if no speciation occur. This is because the enthalpy contributions from speciation and from excess properties have been lumped together in the terms for relative enthalpy. The excess terms are zero in the ideal solution, but speciation still occurs.

In systems where speciation occurs to a significant degree, the excess contribution to the heat of mixing and the heat capacity of electrolyte solutions is usually relatively small compared to the enthalpy effect of speciation. This is illustrated in exercise 8.1.

8.2.1 Heat of dilution

The enthalpy change per mole of salt associated with the dilution of a salt solution from molality m_1 to molality m_2 at constant temperature is the integral heat of dilution, $\Delta H(m_1 \rightarrow m_2)$. This is a measurable quantity and it is related to the apparent relative molal enthalpy L_ϕ of the salt:

$$\Delta H(m_1 \rightarrow m_2) = L_\phi(m_2) - L_\phi(m_1)$$

where $L_\phi(m)$ is the apparent relative molar enthalpy at the molality m . The integral heat of dilution from molality m to infinite dilution becomes:

$$\Delta H(m \rightarrow 0) = L_\phi(0) - L_\phi(m)$$

Sometimes experimental heat of dilution data are extrapolated to infinite dilution by means of the extended Debye-Hückel law or the Hückel equation and presented in the literature as apparent relative molar enthalpy (L_ϕ) data.

The differential heat of dilution is the partial molar relative enthalpy of solvent L_w as defined by equation (8.12). In a differential heat of dilution experiment, a small amount of water is added to a solution of a certain molality. The amount of water added has to be so small that the molality does not change during the experiment. The enthalpy of formation of the original solution is H_1 , the enthalpy of formation of the final solution is H_2 , and the enthalpy of formation of the differential amount of water is $\Delta n_w H_w^0$. The enthalpy change per mol of water added in the experiment is then:

$$\Delta H = \frac{H_2 - H_1 - \Delta n_w H_w^0}{\Delta n_w} = \frac{H_2 - H_1}{\Delta n_w} - H_w^0 = L_w$$

8.2.2 Heat of solution

The integral heat of solution at infinite dilution, $\Delta H^{s,\infty}$ is the molar enthalpy change for the dissolution of crystalline salt in an infinite excess of pure water at constant temperature.

$\Delta H^{s,\infty}$ is defined by

$$\Delta H^{s,\infty} = L_{\varphi}(0) + \sum_i \nu_i H_i^* - H_c^0 \quad (8.22)$$

where H_c^0 is the standard state enthalpy of the pure crystalline salt.

The integral heat of solution, ΔH^s is the molar enthalpy change for dissolving crystalline salt to form a solution of molality m :

$$\Delta H^s = \Delta H^{s,\infty} + L_{\varphi}(m) - L_{\varphi}(0) = L_{\varphi}(m) + \sum_i \nu_i H_i^* - H_c^0 \quad (8.23)$$

The differential heat of solution ΔH^{ds} is the enthalpy change per mole salt dissolved in a solution already containing dissolved salt

$$\Delta H^{ds} = \Delta H^{s,\infty} + \frac{\Delta L_{\varphi}}{\Delta n_s} \rightarrow \Delta H^{s,\infty} + L_s \text{ for } \Delta n_s \rightarrow 0 \quad (8.24)$$

Exercise 8.1

Carbon dioxide is absorbed in an aqueous solution initially containing 1 kg water, 4 mol NH_3 and 0.4 mol CO_2 . The composition of this initial solution after speciation at 25 °C is given in the column marked (1) of Table 8.1. One of the ions formed by speciation in this system is the carbamate ion, NH_2COO^- .

1.6 mol $\text{CO}_2(\text{g})$ is dissolved in the solution at 25 °C. The enthalpy change by this dissolution process was measured to -125.2 kJ. The composition of this solution after speciation at 25 °C is given in the column marked (2) of Table 8.1.

An additional 2 mol $\text{CO}_2(\text{g})$ is added to this solution at 25 °C, resulting in the precipitation of 1.067 mol $\text{NH}_4\text{HCO}_3(\text{s})$. The enthalpy change measured during this process was -125.8 kJ. The composition of this solution after speciation and precipitation is given in the column marked (3) of Table 8.1.

Calculate what part of the enthalpy change that comes from speciation and what part comes from the change in excess enthalpy in the two processes. Do you think the excess enthalpy change is related to the change in ionic strength between the solutions?

Table 8.1: Standard state enthalpy of formation at 25 °C and the composition of the liquid phase for use in exercise 8.1

Species	$\Delta_f H$ kJ/mol	Mol (1)	Mol (2)	Mol (3)
H_2O	-285.83	55.3916	54.42996	51.68698
$\text{NH}_3(\text{aq})$	-80.29	3.22688	0.662624	6.72E-03
$\text{CO}_2(\text{aq})$	-413.8	1.45E-06	1.71E-04	0.106045
$\text{NH}_4^+(\text{aq})$	-132.51	0.489841	2.416015	2.853546
$\text{H}^+(\text{aq})$	0	6.16E-11	8.12E-10	8.4E-08
$\text{OH}^-(\text{aq})$	-230.243	1.15E-04	4.12E-06	1.34E-08
$\text{CO}_3^{2-}(\text{aq})$	-677.14	0.089728	0.416182	0.026832
$\text{HCO}_3^-(\text{aq})$	-691.99	0.026992	0.662286	2.727387
$\text{NH}_2\text{COO}^-(\text{aq})$	-497	0.283279	0.921361	0.072496
$\text{NH}_4\text{HCO}_3(\text{s})$	-849.4			
$\text{CO}_2(\text{g})$	-393.509			

Exercise 8.2:

Show by an energy balance that the enthalpy change per mole of salt associated with the dilution of a salt solution from molality m_1 to molality m_2 at constant temperature is identical to the apparent relative molal enthalpy L_ϕ of the salt solution at molality m_2 minus the apparent relative molal enthalpy of the salt solution at molality m_1 , as stated in equation (8.19). Show also by an energy balance that the integral heat of solution, ΔH° , the enthalpy change for dissolving one mol of crystalline salt to form a solution of molality m is given by equation (8.23).

8.2.3 Measurement of heats of dilution and solution

Heat of dilution (solution) measurements can be performed by mixing known masses of solution and solvent (solute) initially kept in separate compartments in a calorimeter. When mixing the two samples a temperature change is observed. The typical amount of initial solution is 1 kg, the amount of solvent added in one experiment can be up to 1 kg, the temperature change during the mixing process is typically 0.5 to 5 degree. By measuring the heat capacity of the solution, the enthalpy of mixing can be calculated. A newer method involves the use of a heat-flow micro-calorimeter. In this type of calorimeter, continuous streams of electrolyte solution and solvent are mixed in one chamber. A stream of solvent with a flow rate equal to the sum of the above two streams is passing through another chamber. Thermopiles surrounding the two chambers are connected in opposition. The resulting signal from the thermopiles is proportional to the enthalpy of dilution, Busey *et al.* [72] have described such equipment and experiment in detail.

If heat of dilution experiments are carried out by adding very small amounts of solvent, the molality of the salt can be considered constant. The partial molar enthalpy of solvent can be derived from the measured heat effect.

In heat of solution experiments, the integral and the differential heats of solution can be measured. These properties are defined in equations (8.23) and (8.24). By extrapolating the measured data to infinite dilution, the integral heat of solution at infinite dilution can be found.

Heat of dilution experiments yield differences in the apparent relative molar enthalpy L_ϕ of the salt. Heat of solution experiments yield values of the partial molar enthalpy of the salt plus the integral heat of solution at infinite dilution.

In both cases, the Debye-Hückel law is usually being applied for extrapolating the data to infinite dilution in order to calculate the apparent molar relative enthalpy of the salt and the integral heat of solution at infinite dilution.

The partial molar enthalpy of a salt that does not undergo dissociation or hydrolysis is at sufficient dilution given by the extended Debye-Hückel law (6.16). The derivation follows from equation (8.9):

72 Busey R.H., Holmes H.F., and Mesmer R.E., "The enthalpy of dilution of aqueous sodium chloride to 673 K using a new heat-flow and liquid-flow microcalorimeter. Excess Thermodynamic properties and their pressure coefficients", J. Chem. Thermodynamics, volume 16(1984), pp. 343-372.

$$\left[\frac{\partial(\ln \gamma_i^*)}{\partial T} \right]_x = -Z_i^2 \frac{dA}{dT} \frac{I^{1/2}}{1 + BaI^{1/2}} = -\frac{L_i^{D-H}}{RT^2} \quad (8.25)$$

$$\Rightarrow L_S^{D-H} = \sum \nu_i L_i^{D-H} = RT^2 \frac{dA}{dT} \sum \nu_i Z_i^2 \frac{I^{1/2}}{1 + BaI^{1/2}}$$

The temperature derivative of the Debye-Hückel parameter, A , is available from correlations of A as a function of temperature. One such correlation was given in equation (6.72).

The partial molar relative enthalpy of salt can be calculated from equation (8.25) as a function of the ionic strength at concentrations, where the extended Debye-Hückel law is valid.

The Debye-Hückel contribution to the activity coefficient of water was given in equation (6.19). From that expression, the partial molar enthalpy of water in very dilute solutions can be obtained as:

$$\left[\frac{\partial(\ln \gamma_w)}{\partial T} \right]_x = \frac{dA}{dT} \frac{2M_w}{(Ba)^3} \left[1 + BaI^{1/2} - \frac{1}{1 + BaI^{1/2}} - 2 \ln(1 + BaI^{1/2}) \right] = -\frac{L_w^{D-H}}{RT^2} \quad (8.26)$$

$$\Rightarrow L_w^{D-H} = -RT^2 \frac{dA}{dT} \frac{2M_w}{(Ba)^3} \left[1 + BaI^{1/2} - \frac{1}{1 + BaI^{1/2}} - 2 \ln(1 + BaI^{1/2}) \right]$$

According to equation (8.15) the relative enthalpy of the solution is the sum of the partial molar enthalpies:

$$\begin{aligned} nL^{D-H} &= n_w L_w + n_s L_s \\ &= RT^2 \frac{dA}{dT} \left(n_s \sum \nu_i Z_i^2 \frac{I^{1/2}}{1 + BaI^{1/2}} - \frac{2n_w M_w}{(Ba)^3} \left(1 + BaI^{1/2} - \frac{1}{1 + BaI^{1/2}} - 2 \ln(1 + BaI^{1/2}) \right) \right) \\ &= n_s L_\phi^{D-H} \end{aligned} \quad (8.27)$$

The expression for the apparent relative molar enthalpy can be rearranged to:

$$\begin{aligned} L_\phi^{D-H} &= RT^2 \frac{dA}{dT} \sum \nu_i Z_i^2 \left(\frac{I^{1/2}}{1 + BaI^{1/2}} - \frac{1}{I(Ba)^3} \left(1 + BaI^{1/2} - \frac{1}{1 + BaI^{1/2}} - 2 \ln(1 + BaI^{1/2}) \right) \right) \\ &= \frac{\left(3 + 2 \ln(1 + BaI^{1/2}) - 4(1 + BaI^{1/2}) + (1 + BaI^{1/2})^2 \right)}{(BaI^{1/2})^3} RT^2 \frac{dA}{dT} \sum \nu_i Z_i^2 I^{1/2} \\ &= \chi(BaI^{1/2}) RT^2 \frac{dA}{dT} \frac{2}{3} \sum \nu_i Z_i^2 I^{1/2} \\ &= -\nu RT^2 \frac{d(\ln A)}{dT} \left(\ln \gamma_\pm^* + \frac{n_w}{\nu n_s} \ln \gamma_w \right) = -\nu RT^2 \frac{d(\ln A)}{dT} \left(\ln \gamma_\pm^* - \Phi - \frac{n_w}{\nu n_s} \ln x_w \right) \end{aligned} \quad (8.28)$$

$RT^2 dA/dT \sum \nu_i Z_i^2$ is the *Debye-Hückel limiting slope* for relative enthalpy. It is one of the first three expressions in equation (8.28) that is often used for extrapolating the apparent relative molar enthalpy. The rearrangement in the second and the third line is included in order to show how a linear dependence between apparent relative molar enthalpy data and the square root of the ionic strength can be established. The function $\chi(x)$ was defined in equation (6.7).

The simple relation between enthalpy and mean mole fraction activity coefficients is illustrated in the fourth line, Φ is the osmotic coefficient of the solution. If the mean ionic activity coefficient and the osmotic coefficient are known at the same concentrations, the apparent relative molar enthalpy can be calculated from this equation.

Usually, the b parameter is calculated for the specific electrolyte in order to improve the extrapolation. In order to extend the validity of expression (8.28) to the ionic strengths at which heat of dilution and heat of solution experiments take place, an empirical term like $CI+DI^2$ is added to equation (8.28). C and D are parameters to be determined from the experimentally measured enthalpies. An example is shown in Figure 8.1. Experimental values of the apparent relative molar enthalpy of sodium bicarbonate (at 30°C) measured by Leung and Millero [73] fall outside the validity range of the Debye-Hückel law. An equation like (8.28) extended with the term $CI+DI^2$ was used for correlating the data. This equation was assumed to represent the value of the apparent relative molar enthalpy of sodium bicarbonate, also in the concentration range from infinite dilution to the concentrations at which measurements were made.

Figure 8.1 illustrates the concept of Debye-Hückel limiting slope: The data are plotted as a function of the square root of the ionic strength and follow an almost straight line at high dilution. The slope of this straight line is the Debye-Hückel limiting slope.

8.2.4 Measurement of heat capacity

The determination of the apparent molar heat capacity of salts usually includes the determination of the apparent molar volume of the salt. Perron *et al.* [74], describe their method in detail. With a flow microcalorimeter the relative difference in volumetric specific heat σ ($\text{J K}^{-1} \text{cm}^{-3}$) with respect to that of pure solvent, σ^0 is measured. The total heat capacity, C_p for a solution of volume nV is $nV\sigma$. The partial molar heat capacity of pure water is $C_{p,w}^0 = V_w^0 \sigma^0$, where V_w^0 is the standard state molar volume of water. By inserting these expressions in the definition of the apparent molar heat capacity equation one obtains

$$C_{p,\varphi} = \frac{nV\sigma - n_w V_w^0 \sigma^0}{n_s} \quad (8.29)$$

The apparent molar volume is given by:

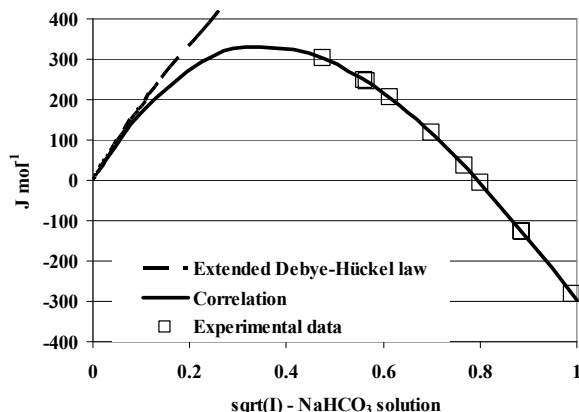


Figure 8.1: The Debye-Hückel apparent relative molar enthalpy of NaHCO_3 at 30°C, compared with experimental data and values calculated with a correlation formed by extending the Debye-Hückel expression for apparent relative enthalpy with a $CI+DI^2$ term.

73 Leung W.H., Millero F.J. "The enthalpy of dilution of some 1-1 and 2-1 electrolytes in aqueous solution". J. Chem. Thermodyn. 7(1975)1067-1078.

74 Perron G., Desnoyers J.E., and Millero F.J., "Apparent molal volumes and heat capacities of alkaline earth chlorides in water at 25°C", Can. J. Chem., volume 52(1974), pp. 3738-3741.

$$V_{\phi} = \frac{nV - n_w V_w^0}{n_s} \quad (8.30)$$

By rearranging, the term for pure water can be expressed by:

$$\frac{n_w V_w^0}{n_s} = \frac{nV}{n_s} - V_{\phi} = \frac{1}{c} - V_{\phi} \quad (8.31)$$

In this equation, c is the molar concentration in mol cm^{-3} . By inserting this expression into equation (8.29), one obtains

$$C_{p,\phi} = V_{\phi} \sigma^0 + \frac{\sigma - \sigma^0}{c} \quad (8.32)$$

Knowing the molar concentration, σ , σ^0 , and V_{ϕ} , the apparent molar heat capacity of a salt can be calculated from equation (8.32). The apparent molar volume can be determined to great accuracy with a flow densimeter.

Apparent molar heat capacity data can be extrapolated to infinite dilution by means of the Debye-Hückel law. The expression follows by differentiation of equation (8.28) with respect to temperature:

$$\begin{aligned} C_{p,\phi}^{D-H} - \sum_i \nu_i C_{p,i}^* &= \frac{dL_{\phi}^{D-H}}{dT} \\ &= \left(2RT \frac{dA}{dT} + RT^2 \frac{d^2 A}{dT^2} \right) \sum_i \nu_i Z_i^2 \left(\frac{I^{1/2}}{1 + BaI^{1/2}} - \frac{\left(1 + BaI^{1/2} - \frac{1}{1 + BaI^{1/2}} - 2 \ln(1 + BaI^{1/2}) \right)}{I(Ba)^3} \right) \\ &= \chi(BaI^{1/2}) \left(2RT \frac{dA}{dT} + RT^2 \frac{d^2 A}{dT^2} \right) \frac{2}{3} \sum_i \nu_i Z_i^2 I^{1/2} \end{aligned} \quad (8.33)$$

$(2RT(dA/dT) + RT^2(d^2 A/dT^2))2/3 \sum \nu_i Z_i^2$ is the Debye-Hückel limiting slope for heat capacity. The function $\chi(x)$ was defined in equation (6.7). Equation (8.33) is usually supplemented with the empirical term $CI + DI^2$ in order to extend its applicability to the concentration range of the experiments. The values of C and D are not equal to those used in the expression for apparent relative molar enthalpy or those used for the activity coefficients.

Exercise 8.3

Jahn and Wolf [75] performed heat of dilution experiments for magnesium chloride solutions, some of their experimental results are given in Table 8.2. The experiments were performed at 25 °C.

Use the data in Table 8.2 to determine a function for the apparent molar enthalpy of magnesium chloride by an expression of the form in (8.28) with an added term $CI + DI^2$. The temperature derivative of the Debye-Hückel parameter A can be determined from equation (6.72). Plot correlated heat of dilution values versus experimental values to show the quality of the fit. What is the enthalpy change per mol salt if a 3 molal solution of magnesium chloride is diluted to 1 molal at 25 °C?

75 H. Jahn, G. Wolf, "The Enthalpy of Solution of MgCl_2 and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in water at 25°C. I. The integral Molar Enthalpy of Solution", J. Solution Chemistry, 22(1993)983-994

Table 8.2: Experimental heat of dilution data at 25 °C for magnesium chloride solutions [75]

Initial molality	Final molality	Enthalpy change J/mol	Initial molality	Final molality	Enthalpy change J/mol
5.700	0.05215	-18500	1.999	0.01752	-6790
5.700	0.04487	-18520	1.999	0.01795	-6760
4.999	0.04448	-16120	1.500	0.009646	-5520
4.954	0.04599	-15860	1.500	0.01501	-5510
4.000	0.03904	-12420	1.500	0.01496	-5550
4.000	0.03424	-12750	1.000	0.01058	-4300
4.000	0.03091	-12710	1.000	0.007961	-4310
3.000	0.02565	-9780	0.800	0.006618	-3940
3.000	0.03011	-9640	0.502	0.005179	-3270
2.499	0.02125	-8080	0.502	0.005069	-3290
2.499	0.02036	-8140			

8.3 Volumetric properties

A considerable volume change takes place when salts are dissolved in water. This effect was called “electrostriction” by Drude and Nernst [76].

The partial molar volume of water can be derived by differentiation of equation (8.6), applied to water, with respect to pressure at constant temperature and composition:

$$\left[\frac{\partial \left(\frac{\mu_w}{RT} \right)}{\partial P} \right]_{T,x} = \left[\frac{\partial \left(\frac{\mu_w^0}{RT} \right)}{\partial P} \right]_T + \left[\frac{\partial \ln \gamma_w}{\partial P} \right]_{T,x} = \frac{V_w}{RT} = \frac{V_w^0}{RT} + \frac{V_w^{ex}}{RT} \quad (8.34)$$

V_w is the partial molar volume of water at the specified composition. V_w^0 is the standard state molar volume of pure water and V_w^{ex} is the excess volume of water. A similar result is obtained for the ions by differentiation with respect to pressure of equation (8.8) at constant temperature and composition:

$$\left[\frac{\partial \left(\frac{\mu_i}{RT} \right)}{\partial P} \right]_{T,x} = \left[\frac{\partial \left(\frac{\mu_i^*}{RT} \right)}{\partial P} \right]_T + \left[\frac{\partial \ln \gamma_i^*}{\partial P} \right]_{T,x} = \frac{V_i}{RT} = \frac{V_i^*}{RT} + \frac{V_i^{ex}}{RT} \quad (8.35)$$

V_i is the partial molar volume of solute i in the solution. V_i^* is the standard state partial molar volume of ion i and V_i^{ex} is the excess volume of ion i . The standard state partial molar volume of a solute is the same in the unsymmetrical mole fraction system and in the molality based system because the difference between the corresponding standard state chemical potentials is independent of pressure.

76 Drude P. and Nernst W., “Über elektrostriktion durch freie Ionen”, Z. phys. Chemie 15(1894)75-85

Similar to the thermal properties derived from the chemical potentials at constant pressure and composition, equation (8.34) and (8.35) are only correct for systems in which there is no speciation. Speciation equilibria are dependent of pressure as described in section 7.7. The composition of a system in which speciation is taking place can therefore not be held constant while making the pressure derivative. The composition change with pressure does not have as significant an effect on the volume as the composition change with temperature has on enthalpy. The effect of the composition change due to the pressure change will therefore be ignored here.

The apparent molar volume $V_{\phi,S}$ of a salt is:

$$V_{\phi,S} = \frac{nV - n_w V_w^0}{n_S} \quad (8.36)$$

$nV = n_w V_w + n_S \sum v_i V_i$ is the total volume of the solution and V_w^0 is the standard state molar volume of water.

Masson [77] discovered in 1929 that the apparent molar volumes of salts often are linear functions of the square root of the molar concentration in the concentration range from infinite dilution to saturation of the salt:

$$V_{\phi,S} = V_S^* + k\sqrt{c} \quad (8.37)$$

In this equation, the molar concentration is usually given as mol/liter solution and the units of k are further adjusted so that the apparent molar volume is expressed in cubic centimeter per mol salt.

Two years later, Redlich [78] showed that this relation can be derived theoretically. The theoretical relation was derived by differentiating the limiting law of Debye-Hückel with respect to pressure. This leads to:

$$V_{\phi,S} = V_S^* + q \left(\frac{1}{2} \sum v_i Z_i^2 \right)^{3/2} \sqrt{c} \quad (8.38)$$

The factor q is determined from the Debye-Hückel limiting law.

The excess Gibbs energy function according to the Debye-Hückel limiting law is given in equation (6.20). In order to calculate the excess volume as the pressure derivative of this excess Gibbs energy function, molarity was re-introduced into the equation for the excess Gibbs energy. In the limit of infinite dilution, where this equation is valid, molarity and molality are almost equal numerically. A significant advantage of the molality concentration scale compared to the molarity scale is that it is independent of temperature and pressure. For the purpose of deriving the excess volume from the excess Gibbs energy function, molarity was re-introduced in order to recover this pressure dependence. The equation used for the excess Gibbs energy of the Debye-Hückel limiting law written in terms of the molarity concentration scale is:

$$G_{Debye-H\ddot{u}ckel\ limiting\ law}^{ex} = -\frac{1}{3} RT \sum x_i z_i^2 s \kappa \quad (8.39)$$

77 Masson D.O., "Solute molecular volumes in relation to solvation and ionization", Philosophical Magazine and journal of Science, 8(1929)218-235

78 Redlich O., and P. Rosenfeld, "Das partielle molare Volumen von gelösten Elektrolyten. I.", Z. physikal. Chem. Abt. A., 155(1931)65-74

According to equations (6.5) and (6.6), the product $s\kappa$ is given by:

$$s\kappa = \frac{F^2}{4\pi N_A \epsilon_0 \epsilon_r RT} \frac{1}{\left(\frac{F^2}{\epsilon_0 \epsilon_r RT} \frac{\sum n_i z_i^2}{nV} \right)^{1/2}} = \frac{F^3}{4\pi N_A} \left(\frac{1}{\epsilon_0 \epsilon_r RT} \right)^{3/2} \left(\frac{\sum n_i z_i^2}{nV} \right)^{1/2} \quad (8.40)$$

The pressure derivative of the excess Gibbs function for the Debye-Hückel limiting law is caused by the pressure dependence of the relative permittivity of water and the pressure dependence of the volume of the solution. Equation (8.40) is modified to give:

$$s\kappa = \left(s\kappa \epsilon_r^{3/2} V^{1/2} \right) \epsilon_r^{-3/2} V^{-1/2} \quad (8.41)$$

The term in the bracket is independent of pressure. This expression for $s\kappa$ is inserted into equation (8.39) and is differentiated with respect to pressure:

$$\begin{aligned} \left[\frac{\partial (nG_{Debye-H\ddot{u}ckel\ limiting\ law}^{ex})}{\partial P} \right]_{T,x} &= -\frac{1}{3} RT \sum n_i z_i^2 \left[\frac{\partial (s\kappa)}{\partial P} \right]_{T,x} \\ &= \frac{1}{3} RT \sum n_i z_i^2 \left(s\kappa \cdot \epsilon_r^{3/2} V^{1/2} \right) \left(\frac{3V^{-1/2}}{2\epsilon_r^{5/2}} \frac{d\epsilon_r}{dP} + \frac{\epsilon_r^{-3/2}}{2V^{3/2}} \frac{dV}{dP} \right) \\ &= \frac{1}{3} RT \sum n_i z_i^2 s\kappa \left(\frac{3}{2} \frac{1}{\epsilon_r} \frac{d\epsilon_r}{dP} + \frac{1}{2} \frac{1}{V} \frac{dV}{dP} \right) \\ &= \frac{s\kappa}{2} \left[\frac{d \ln \epsilon_r}{dP} - \frac{\alpha}{3} \right] RT \sum n_i z_i^2 \\ &= nV^{ex} \end{aligned} \quad (8.42)$$

Here, the isothermal compressibility for pure water, α has been introduced. The excess volume calculated in equation (8.42) can be used for expressing the apparent molar volume of the salt according to equation (8.5):

$$\begin{aligned} V_{\phi,S} &= V_S^* + \frac{nV^{ex}}{n_S} \\ &= V_S^* + \frac{\frac{s\kappa}{2} \left[\frac{d \ln \epsilon_r}{dP} - \frac{\alpha}{3} \right] RT \sum n_i z_i^2}{n_S} \\ &= V_S^* + \frac{\frac{1}{2} \frac{F^3}{4\pi N_A} \left(\frac{1}{\epsilon_0 \epsilon_r RT} \right)^{3/2} \left(\frac{\sum n_i z_i^2}{nV} \right)^{1/2} \left[\frac{d \ln \epsilon_r}{dP} - \frac{\alpha}{3} \right] RT \sum n_i z_i^2}{n_S} \\ &= V_S^* + \frac{F^3}{\pi N_A} \left(\frac{1}{8RT (\epsilon_0 \epsilon_r)^3} \right)^{1/2} c^{1/2} \left[\frac{d \ln \epsilon_r}{dP} - \frac{\alpha}{3} \right] \left(\frac{1}{2} \sum v_i z_i^2 \right)^{3/2} \end{aligned} \quad (8.43)$$

In equation (8.43), the molar concentration of salt, c mol/liter has been introduced. The final result corresponds to equation (8.38) with

$$q = \frac{F^3}{\pi N_A} \left(\frac{1}{8RT (\epsilon_0 \epsilon_r)^3} \right)^{1/2} \left[\frac{d \ln \epsilon_r}{dP} - \frac{\alpha}{3} \right] \quad (8.44)$$

At 25 °C, the parameter q has the value 1.885 for use with c in mol/liter and yielding volumes in cm^3/mol .

For the practical purpose of correlating the density of an electrolyte solution however, “Masson's rule” equation (8.37) usually gives far better results than the theoretical equation (8.38). This is especially true for concentrated solutions as evidenced by Figure 8.2. The Debye Hückel limiting law however is considered most suitable for estimating the partial molar volume of electrolytes at infinite dilution. This is consistent with the fact that the Debye-Hückel limiting law gives correct results for the activity coefficients in very dilute electrolyte solutions. This is an equation for the electrostatic interactions between ions in extremely dilute solutions that are otherwise ideal [79].

Apparent molar volumes of ions are often considered additive. A good approximation for the density of multi component electrolyte solutions can thus be obtained by adding the individual ionic contributions to the apparent molar volume:

$$nV = n_w V_w^0 + \sum_i n_i V_{\phi,i} \quad (8.45)$$

It was shown by Christensen [80] that densities of multi component electrolyte solutions can be calculated accurately from equation (8.45) when the apparent molar volume of ion i , $V_{\phi,i}$ is calculated at the ionic strength of the solution:

$$V_{\phi,i} = V_{\phi,i}^* + k_i \sqrt{I} \quad (8.46)$$

$V_{\phi,i}^*$ is the temperature dependent standard state molar volume of the ion i . I is the ionic strength in mol/(kg water). The temperature dependence of the standard state molar volume of an ion is calculated by:

$$V_{\phi,i}^* = V_{\phi,i,T=298.15}^* + v_{2i}(t - 25) + v_{3i}(t - 25)^2 \quad (8.47)$$

The proportionality factor k_i from equation (8.46) is also determined as a function of temperature.

$$k_i = k_{1i} + k_{2i}(t - 25) + k_{3i}(t - 25)^2 \quad (8.48)$$

For each ion, there are thus 5 adjustable parameters that can be determined from experimental density data. Parameters for a number of ions were determined by Christensen. Some of these parameters are given in Table 8.3. The parameters are based on binary data for only the

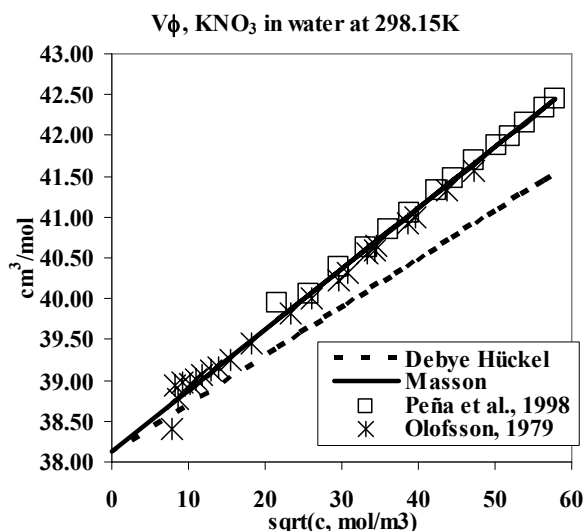


Figure 8.2: Apparent molar volume of potassium nitrate solutions calculated with the Debye-Hückel equation, and with Masson's rule, compared with experimental data.

79 Redlich O., Meyer D.M., “The molal volume of electrolytes”, Chemical Reviews, 64(1964)221-227

80 Christensen S.G., “Thermodynamics of Aqueous Electrolyte Solutions – Application to Ion Exchange Systems”, Ph.D. Thesis, Department of Chemical Engineering, Technical University of Denmark (2004)

following salts in water: NaCl, NaNO₃, Na₂SO₄, KCl, HCl, NH₄Cl, CaCl₂, MgCl₂. The results for salts like Mg(NO₃)₂, MgSO₄, Ca(NO₃)₂, (NH₄)₂SO₄ and more are therefore predictions based on the assumption of the additivity of apparent molar volumes. Some results concerning 1-2 and 2-2 salts at 25 °C are shown in Figure 8.3.

These parameters are valid in the temperature range from 0 to 100 °C. The accuracy decreases with increasing concentration. The standard state molar volumes of ions given in Table 8.3 were taken from Marcus [81] after proper adjustment so that the standard state molar volume of the hydrogen ion is equal to zero cm³/mol.

Table 8.3: Standard state molar volumes and parameters used for determining the volume of aqueous electrolyte solutions using equations (8.45) to (8.48) [80]. The standard state molar volumes are given in cm³/mol and the parameters are given for calculation of apparent molar volumes in cm³/mol.

	$V_{\phi,i,T=298.15\text{ K}}^*$	$v_{2i} \cdot 10^2$	$v_{3i} \cdot 10^4$	k_{1i}	$k_{2i} \cdot 10^2$	$k_{3i} \cdot 10^4$
H ⁺	0	0	0	0	0	0
Na ⁺	-1.2	7.748	-13.80	0.9758	-2.628	6.309
K ⁺	9	6.331	-7.502	1.094	-2.689	3.919
Mg ²⁺	-21.2	1.096	-9.093	1.493	-2.144	4.751
Ca ²⁺	-17.9	-1.938	2.789	1.581	3.450	-5.821
NH ₄ ⁺	18.2	1.604	-1.957	0.4435	-0.7984	0.5941
Cl ⁻	17.8	3.692	-7.407	0.9454	-0.0979	0.9162
SO ₄ ²⁻	14	13.36	-27.39	4.837	-2.927	6.793
NO ₃ ⁻	29	10.78	-4.537	1.307	-2.751	0.0439

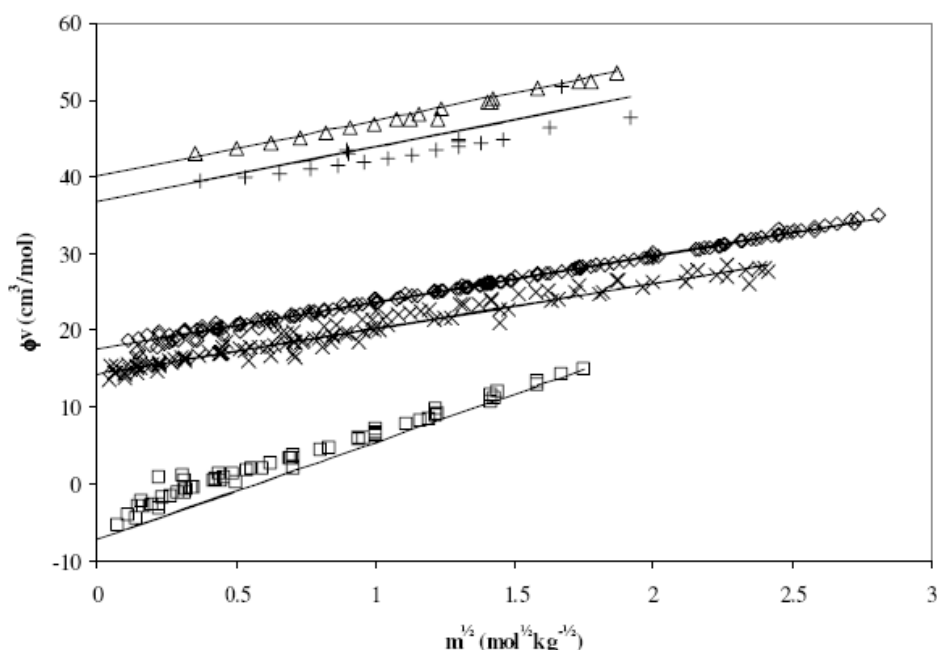


Figure 8.3: Apparent molar volumes of CaCl₂ (◇), Ca(NO₃)₂ (Δ), MgCl₂ (×), Mg(NO₃)₂ (+), and MgSO₄ (□) at 25 °C. The lines are based on the correlation in equation (8.46). Of these data, only those for CaCl₂ and MgCl₂ were used for parameter estimation [80].

Other models for the density of electrolyte solutions include the semi-empirical model of Söhnle and Novotny [82] valid for a large number of electrolytes in a temperature range that spans from 0 to 100 °C for most electrolytes. Another density model was developed by Krumgalz et al. [83] by adding pressure and temperature dependent parameters to the Pitzer model. This model is valid in the temperature range from 15 to 95 °C.

Exercise 8.4

Calculate the densities of H₂O-Na₂SO₄-MgSO₄ mixtures at 50 °C. At this temperature the density of water is 988 kg/m³. Compare the results with the densities measured by Benrath *et al.*[84] in saturated solutions. These data are given in Table 8.4. Try to explain the shape of the graph when you plot the density as a function of the fraction (gram Na₂SO₄)/(gram Na₂SO₄ + gram MgSO₄).

Table 8.4: Densities of saturated solutions of Na₂SO₄ and MgSO₄ at 50 °C.

Mass % Na ₂ SO ₄	Mass % MgSO ₄	Density, g/cm ³	Mass % Na ₂ SO ₄	Mass % MgSO ₄	Density, g/cm ³
31.70	0.00	1.31	16.75	17.10	1.373
30.20	1.84	1.326	14.81	19.05	1.379
29.42	3.52	1.329	13.86	20.16	1.38
25.64	8.68	1.363	9.91	24.45	1.4
24.77	9.80	1.364	7.55	27.49	1.414
23.25	11.98	1.381	4.74	31.32	1.428
22.64	12.56	1.38	3.95	31.60	1.426
18.62	15.75	1.374	1.96	32.50	1.41
			0.00	33.50	1.401

82 Söhnle, O.; Novotny, P. *Densities of Aqueous Solutions of Inorganic Substances*, Phys. Sci. Data 22; Elsevier: Tokyo, 1985.

83 Krumgalz, B.S; Pogorelskii, R.; Sokolov, A.; Pitzer, K.S. "Volumetric Ion Interaction Parameters for Single-Solute Aqueous Electrolyte Solutions at Various Temperatures", J. Phys. Chem. Ref. Data. 29(2000)1123-1140.

84 Benrath A., Pitzler H., Ilieff N., Beu W., Schloemer A., Clermont J., Kojitsch, Benrath H., "Über das reziproke Salzpaar MgSO₄-Na₂(NO₃)₂-H₂O. I", Z. Anorg. Chem. 170(1928)257-287

9 Phase diagrams

An important function of phase diagrams is to be a visual tool for verifying the calculations and predictions of a thermodynamic model by comparing calculated phase diagrams with experimental ones.

Phase diagrams are also important tools when designing fractional crystallization processes. Information on which salt(s) can be encountered in a given electrolyte system as a function of temperature is important for the design of such processes. Also the process paths for fractional crystallization processes can be displayed in phase diagrams. Phase diagrams may thus be used to verify and analyze process simulation and optimization results. For systems with more than four ions however, the use of phase diagrams becomes impractical.

9.1 Phase rule and invariant points

According to Gibbs phase rule, a system with C chemically independent components and P phases in equilibrium has $F=C-P+2$ degrees of freedom. For a system consisting of one pure species the phase rule is $F=3-P$. If two phases are in equilibrium with each other in a one-component system, the system has one degree of freedom. The system is univariant.

Pure water represents a one component system. Pure water boils at 100°C if the pressure is one atmosphere. If the pressure is lower than one atmosphere, pure water will boil at a temperature below 100°C . If the pressure is higher than one atmosphere, pure water will boil at a temperature higher than 100°C . A one component system consisting of water vapor in equilibrium with liquid water has only one degree of freedom. The pressure or the temperature can be fixed. Fixing one will automatically determine the other.

At the triple point of water, ice, water, and steam are in equilibrium. According to the phase rule, a one component system has no degree of freedom when three phases are in equilibrium ($F=0$). The system is invariant. The triple point of water is at 273.16 K and 612 Pa .

An aqueous solution of a pure salt contains three species: water, cations and anions. Still there are only two chemically independent components as the charge of the cations has to be balanced with an equivalent charge of the anions. The solution is therefore considered a binary solution, a solution of two chemically independent components. The phase rule is $F=4-P$ for this system. An invariant point in a binary system thus is a point where 4 phases are in equilibrium (two salts, liquid, and vapor). In a ternary system 5 phases are in equilibrium in an invariant point.

9.2 Binary phase diagram

The Calcium Chloride - water system is here used as an example of a binary phase diagram. The diagram is shown in Figure 9.1.

Pure water freezes to ice at 0°C . If CaCl_2 is added to water, the freezing point of the solution will be lower than 0°C due to the freezing point depression. As the graph shows, ice will form at -20°C in a 20 mass % solution of CaCl_2 .

A solution containing 31 mass % CaCl_2 has the lowest freezing point of any CaCl_2 solution (about -50°C). This solution is called a eutectic solution. The point (A) in the diagram marks the freezing point of this solution. This is a eutectic point, also called a cryohydric or cryohydratic point.

At the freezing point of an eutectic CaCl_2 solution, the solution is in equilibrium with two

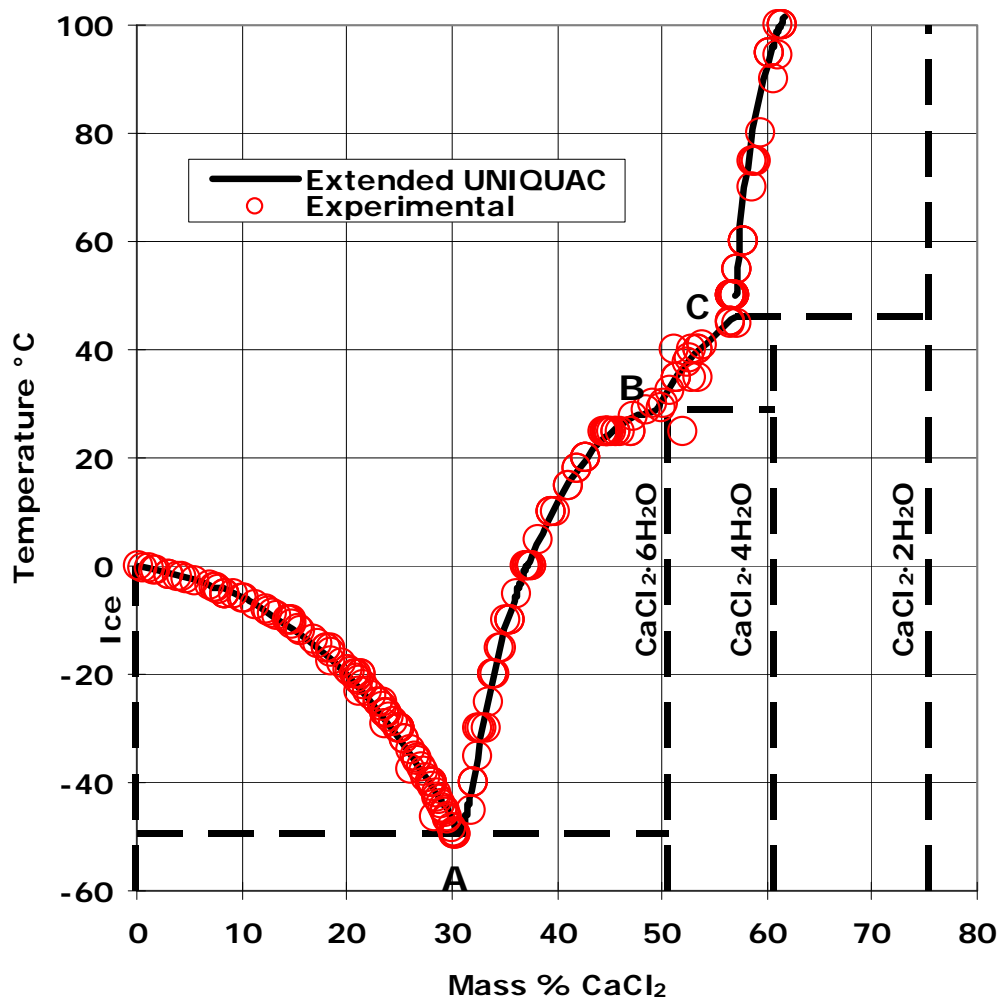


Figure 9.1: Solubility diagram for the $\text{CaCl}_2 - \text{H}_2\text{O}$ system.

solid phases: ice and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Counting also the vapor phase, a total of four phases are in equilibrium in this binary system. The eutectic point therefore constitutes an invariant point.

On the curve between the points A and B the solid phase precipitating from saturated solutions will be the hexahydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

Between B and C the solid phase will be the tetrahydrate, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$. At higher concentrations the dihydrate, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and the anhydrate CaCl_2 will precipitate (not shown in the diagram).

The points B and C are peritectic points. In a peritectic point, a solid phase changes upon heating into a liquid in equilibrium with another solid phase. $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ consists of 60.6 mass percent CaCl_2 . This composition is marked with a vertical dashed line in Figure 9.1. If $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ is heated to 45.3°C it will decompose into a liquid in equilibrium with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at the point C. The temperature at which this happens is marked with a horizontal dashed line.

The two points B and C represent solutions in equilibrium with two solid phases and a gas phase and therefore constitute invariant points.

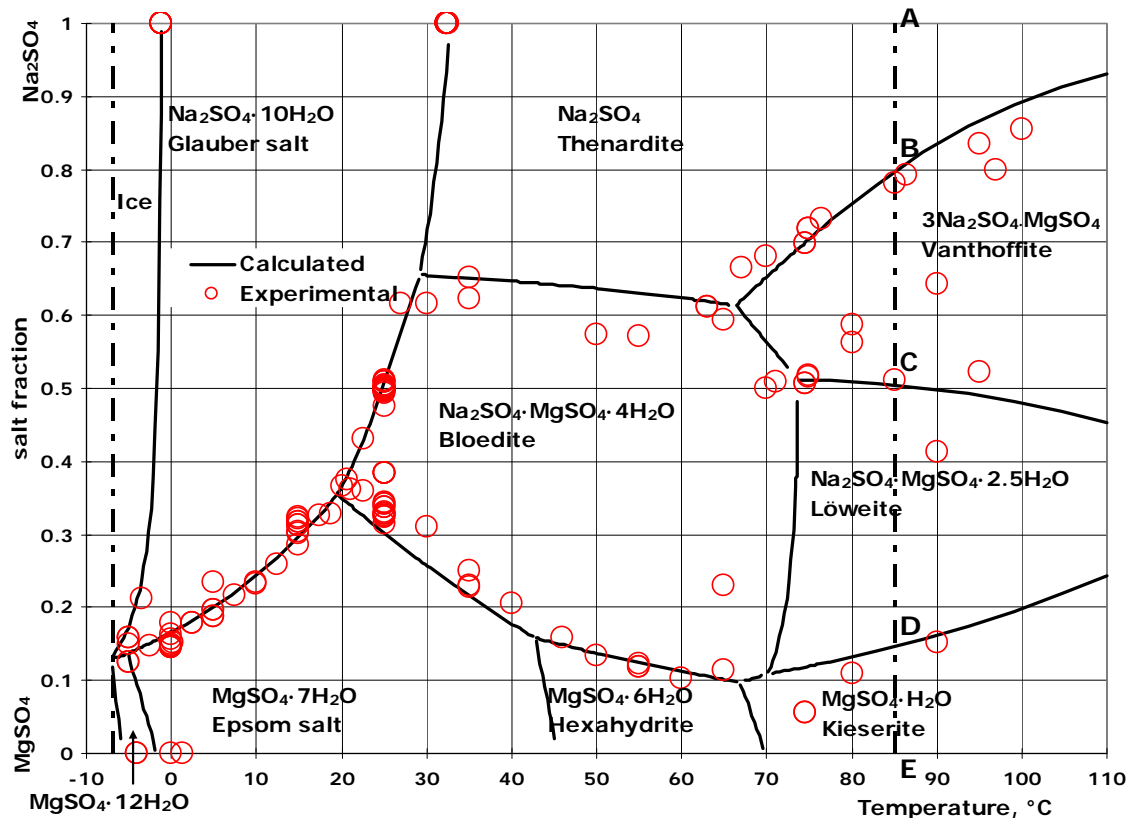


Figure 9.2: Phase diagram for the $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ system in the temperature range from the eutectic temperature (-7°C) to 110°C .

9.3 Ternary phase diagram

In the ternary system consisting of water, sodium sulfate, and magnesium sulfate, the following solid phases appear in the temperature range from -10 to 110°C :

- Ice
- $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, glauber's salt
- Na_2SO_4 , thenardite
- $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, magnesium sulfate dodecahydrate
- $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, epsom salt
- $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, hexahydrate
- $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, kieserite
- $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, bloedite
- $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2.5\text{H}_2\text{O}$, löweite
- $3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$, vanthoffite

The ternary diagram shown in Figure 9.2 has the temperature as abscissa and gives a quick overview of the temperature ranges and concentration ranges (dry basis) at which each of the salts are found. This is essential information if for example you are asked to produce vanthoffite from a ternary solution of sodium sulfate, magnesium sulfate and water.

All fields in Figure 9.2 represent solutions saturated with one solid. The equilibrium lines and the experimental data in the diagram represent compositions and temperatures at which two

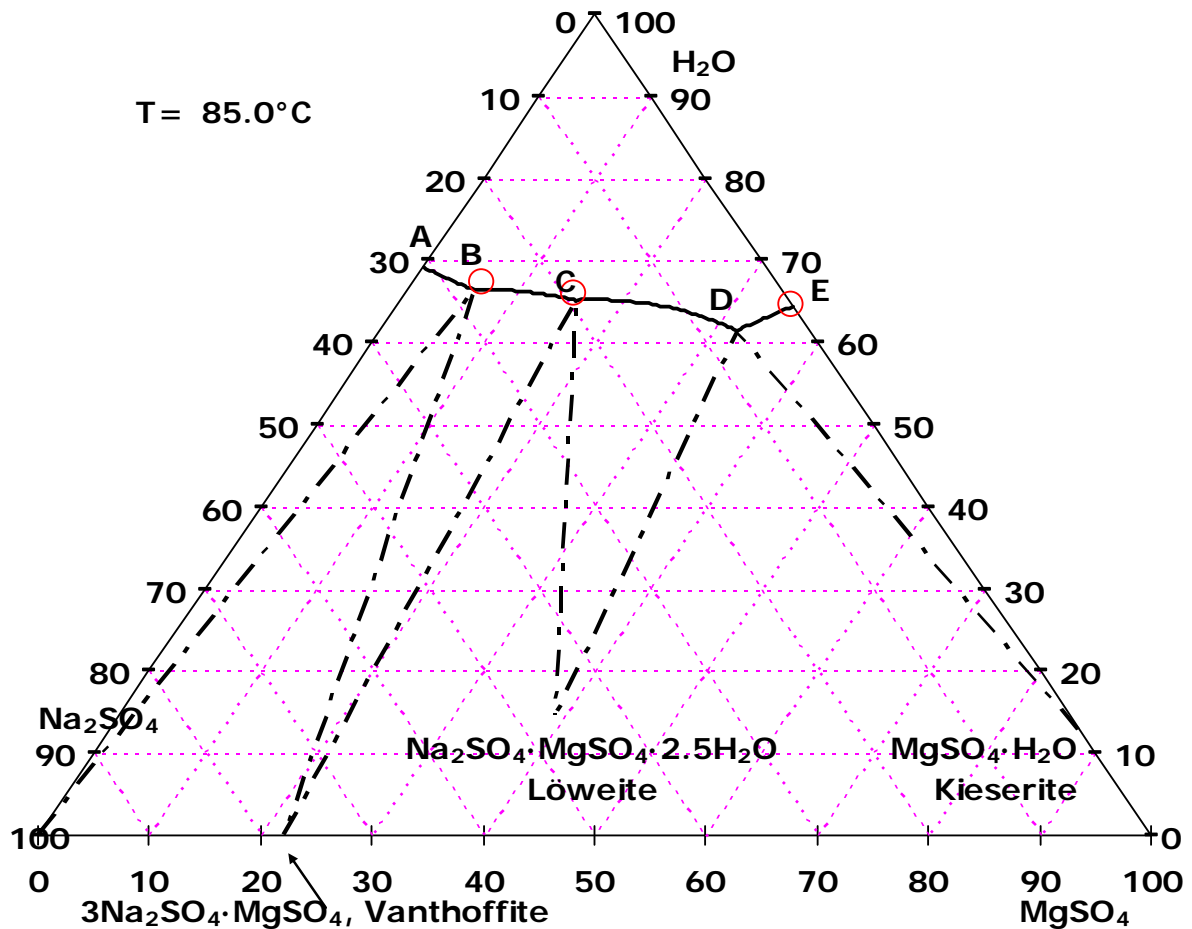


Figure 9.3: The 85°C Isotherm for the $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{MgSO}_4$ system. Tie lines are marking the four solid phases formed in the system at this temperature. The concentrations are in mass %.

solid phases are in equilibrium with the same liquid. At the points, where the phase diagram lines meet, three solids are in equilibrium with the same liquid and with a gas phase. In a ternary system, the phase rule $F=5-P$. The number of degrees of freedom in these points is therefore 0. They are invariant points.

At -7°C a vertical dashed line is marked. This is the eutectic temperature for this ternary system. At this temperature 5 phases are in equilibrium: Ice, $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, liquid and gas. At temperatures lower than -7°C , the solution will split into solid phases of Ice, $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

The ordinate in the diagram Figure 9.2 is “salt fraction” which here is defined as $\text{mol Na}_2\text{SO}_4$ divided by $(\text{mol Na}_2\text{SO}_4 + \text{mol MgSO}_4)$. In this diagram it is not possible to see the water content of the equilibrium solutions. In order to see the water content, an isotherm for the system can be calculated. The 85°C isotherm is marked in Figure 9.2. It passes through 4 different solubility fields from A to E.

Figure 9.3 shows the 85°C isotherm for the same system. The points A to E equivalent with the corresponding points in Figure 9.2 are marked on the equilibrium curve. On the equilibrium curve from A to B, solutions are in equilibrium with Na_2SO_4 . All solutions with a gross composition in the nearly triangular area from A to B to Na_2SO_4 are supersaturated with Na_2SO_4 . After Na_2SO_4 has precipitated from these solutions and phase equilibrium is

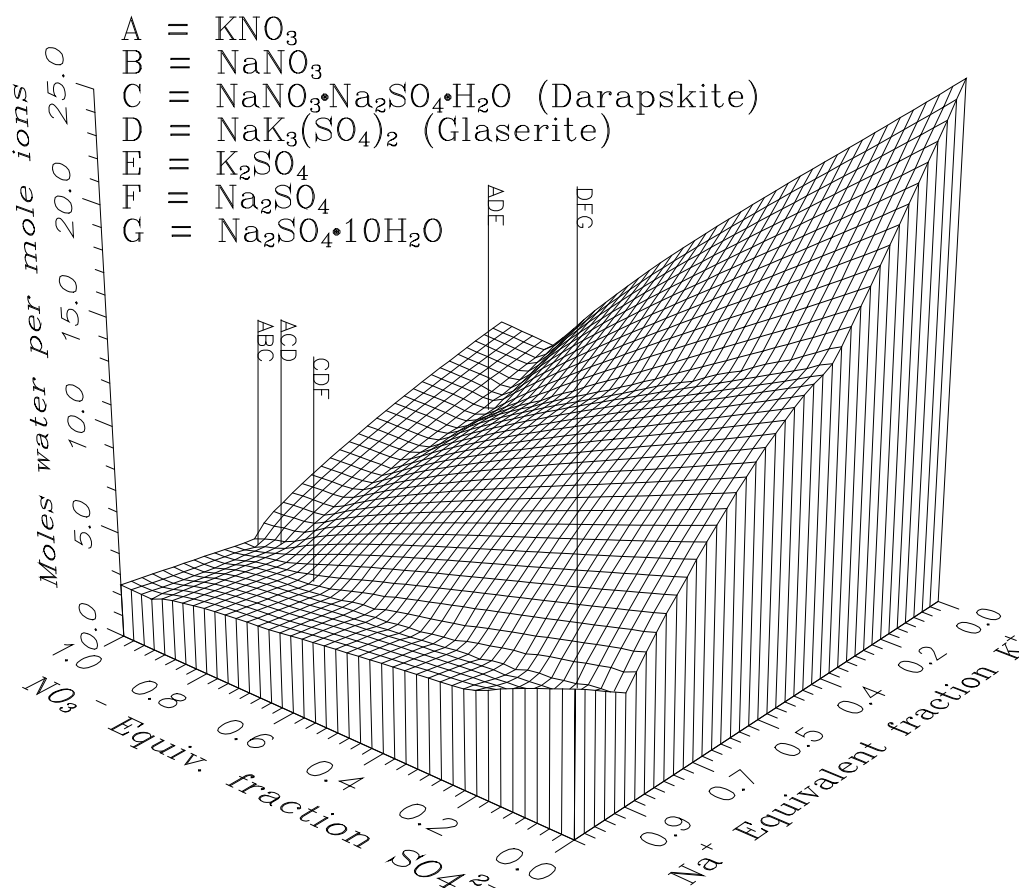


Figure 9.4: Phase diagram for the quaternary NaNO₃ – K₂SO₄ – H₂O system at 30°C

achieved, the composition of the liquid will be on the line from A to B. From B to C solutions are in equilibrium with vanthoffite. In the triangular area marked by B, Na₂SO₄, and vanthoffite, all solutions are supersaturated with both Na₂SO₄ and vanthoffite. At equilibrium all these solutions will have the same liquid composition, B, as this is the only composition, which can be in equilibrium with both salts at this temperature.

9.4 Quaternary systems

Figure 9.4 shows the three dimensional quaternary phase diagram for the (Na⁺, K⁺, NO₃⁻, SO₄²⁻, H₂O) system at 30°C. This type of diagram is not very practical to work with due to its three dimensions. Figure 9.5 shows the same diagram as a Jänecke projection [85]. At all grid intersections, the number of moles water per mole of ions is indicated. In this way, Figure 9.5 provides the same information as Figure 9.4, and is much easier to work with.

For quaternary systems with either three anions and one common cation or three cations and one common anion the quaternary phase diagram becomes triangular. The calculation of curve intersections and curves in this sort of diagrams follows the same pattern as described above for the quadratic phase diagram.

85 Jänecke E., "Über eine neue Darstellungsform der wässerigen Lösungen zweier und dreier gleichioniger Salze, reziproker Salzpaare und der van't Hoff'schen Untersuchungen über ozeanische Salzablagerungen", Z. anorg. Chemie, 51(1906)132-157.

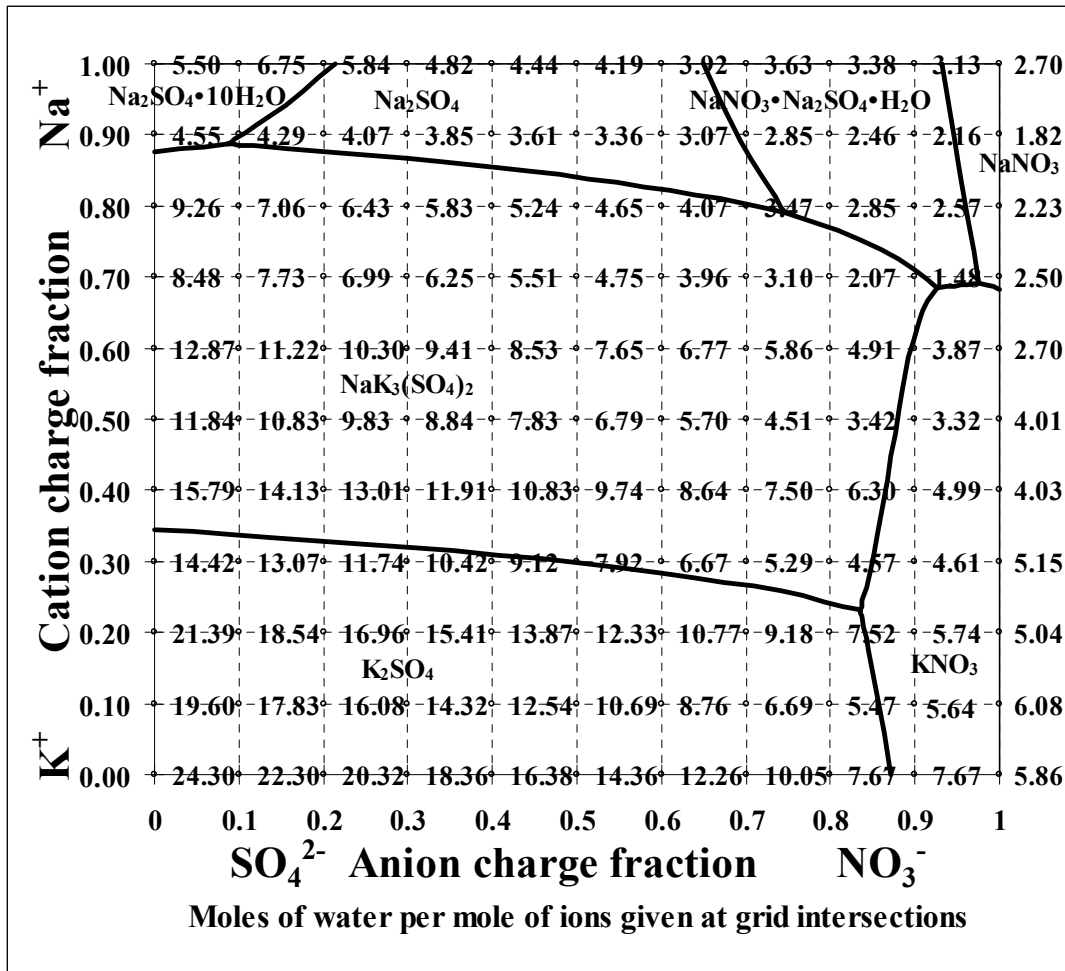


Figure 9.5: Jänecke projection of the phase diagram for the quaternary $\text{NaNO}_3 - \text{K}_2\text{SO}_4 - \text{H}_2\text{O}$ system at 30°C

The abscissa in Figure 9.4 and Figure 9.5 is the charge or equivalent fraction of the NO_3^- ion,

calculated as $X = \frac{n_{\text{NO}_3^-}}{n_{\text{NO}_3^-} + 2n_{\text{SO}_4^{2-}}}$, where n is the number of moles of the ion indicated. The

factor 2 on the number of moles of sulfate ion is included because each sulfate ion carries a charge of -2.

The ordinate in the diagrams is the charge or equivalent fraction of the K^+ ion, calculated as

$Y = \frac{n_{\text{K}^+}}{n_{\text{K}^+} + n_{\text{Na}^+}}$. The corner in the foreground of Figure 9.4 has the coordinates (0,1) and

therefore corresponds to the upper left corner of Figure 9.5.

Exercise 9.1:

Based on the experimental data in Table 9.1, valid at 100°C , construct a triangular diagram like the one in Figure 9.3. Include the tie-lines and the names of the solid phases at the appropriate places in the diagram.

Mark in the diagram the composition of a super-saturated solution with the total mass of 1000 gram from which 200 gram of wegscheiderite, $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ will precipitate.

Mark also the composition of a super-saturated solution with a total mass of 1000 gram from which 200 gram of trona, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ and 200 gram of sodium carbonate monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ will precipitate.

Table 9.1: Solid-liquid equilibrium data for the ternary Na_2CO_3 - NaHCO_3 - H_2O system at 100 °C. The data were measured by Waldeck et al. [86]

Mass percent		Solid Phase(s)
Na_2CO_3	NaHCO_3	
30.7	0	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
29.9	2.3	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
29.2	3.4	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
29.1	4.2	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
27.9	5.2	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
27.7	5.3	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
26.7	5.9	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
25.3	7.1	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
25.1	7.2	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
23.6	8.2	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
22.7	8.8	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
21.1	9.7	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$
21	9.8	$\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$
19.3	10.7	$\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$
16.5	11.9	$\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$
13.4	14.4	$\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$
12.7	14.4	$\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$ and NaHCO_3
8.7	16	NaHCO_3
1.2	18.5	NaHCO_3

Exercise 9.2

Data for phase equilibrium in the quaternary $\text{H}_2\text{O} - (\text{Na}^+ - \text{Mg}^{2+}) - (\text{Cl}^- - \text{SO}_4^{2-})$ system are given in Table 9.2. The data come from two different sources. The solid phases are indicated with letters A to G. The meaning of these letters is given in the bottom left part of the table.

Construct a Jänecke diagram similar to the one in Figure 9.5 from these data. Do not include the water content, only the projection. Sketch how you think the phase diagram lines will pass through the experimental points and write on the diagram what solid phases precipitate in the various fields. Determine if the data from the two sources are in agreement with each other.

Table 9.2: Experimental data for phase equilibrium in the $\text{H}_2\text{O} - (\text{Na}^+ - \text{Mg}^{2+}) - (\text{Cl}^- - \text{SO}_4^{2-})$ system at 25 °C.

Data from Visyagin [87], mass %					Data from Pel'sh [88], mass %				
NaCl	Na_2SO_4	MgCl_2	MgSO_4	Solid phases	NaCl	Na_2SO_4	MgCl_2	MgSO_4	Solid phases
14.41	15.01	0	0	A B	22.85	6.91	0	0	C A

86 Waldeck W.F., Lynn G., Hill A.E., "Aqueous solubility of salts at high temperatures II. The ternary system Na_2CO_3 - NaHCO_3 - H_2O from 100 – 200 °C", J. Am. Chem. Soc., 56(1934)43-47

87 Visyagin, N.I., "Chemical Concentration and Refraction of Mixtures, The reciprocal salt pairs MgSO_4 , Na_2Cl_2 , MgCl_2 , Na_2SO_4 at 25 °C", Bull. Inst. Galurgie, (1939)18-28 (10-11)

88 Pel'sh, A.D., "Solubility Diagram for the Reciprocal System Na_2SO_4 , MgCl_2 , NaCl , MgSO_4 at 25 °C", Tr. Vses Nauch.-Issled. Inst. Galurgii, 27(1953)3-16

13.68	15.13	0	1.58	A	B		20.73	7.63	1.45	0	C	A	
12.31	13.5	0	2.77	A	B		15.35	9.98	5.05	0	C	A	
11.81	15.91	0	3.61	A	B		15.19	10.1	5.21	0	C	A	
10.18	15.79	0	5.84	A	B		13.92	10.55	5.99	0	C	A	G
9.41	15.85	0	6.92	A	B		13.92	10.55	5.99	0	C	A	G
9	16.56	0	7.27	A	B		9.12	15.26	5.99	0	A	G	
7.96	15.84	0	9.42	A	B	G	5.95	18.75	6.15	0	A	G	
7.27	15.95	0	9.55	A	B	G	3.96	21.08	6.38	0	A	G	
22.74	1.8	0	7.82	C	A	G	0	25.05	6.22	1.34	A	G	B
23.31	3.49	0	8.76	A	G		14.05	14.94	0	0	A	B	
18.74	4.94	0	7.62	A	G		7.6	19.88	3.17	0	A	B	
15.83	6.46	0	8.51	A	G		5.87	21.28	4.03	0	A	B	
12.09	11.58	0	8.36	A	G		4.02	22.79	4.9	0	A	B	
3.5	19.21	0	12.67	B	G		1.1	24.71	6.11	0	A	B	
1.96	19.73	0	13.81	B	G		1.19	24.97	6.27	0	A	B	
0	18.89	0	15.34	B	G		1.15	24.98	6.3	0	A	B	
1.81	18.62	0	8.22	B			0	25.05	6.22	1.34	A	B	G
6.61	16.29	0	7.02	B			0	24.64	5.72	2.87	A	B	
7.94	15.51	0	8.41	B			0	19.12	0	15.64	B	G	
9.07	14.56	0	9.5	B			0	20.97	1.96	11.04	B	G	
0.99	15.56	0	0.54	B			0	21.77	2.63	9.26	B	G	
3.38	19.21	0	1.98	B			0	23.06	3.89	6.39	B	G	
7.7	15.78	0	3.5	B			0	24.14	5.25	3.42	B	G	
4.73	18.43	0	1.38	B			0	25.05	6.22	1.34	G	B	A
7.9	15.69	0	2.47	B			0	12.36	0	21.79	E	G	
9.61	15.54	0	3.02	B			0	10.92	5.41	14.9	E	G	
10.8	15.39	0	3.41	B			0	9.72	13.58	5.69	E	G	
11.41	15.28	0	3.55	B	A		0	8.77	17.16	3.12	E	G	
12.12	15.18	0	3.6	B	A		0	6.76	20.89	1.98	C	E	G
12.05	15.37	0	4.05	A			0	7.28	20.55	1.93	C	E	
13.53	12.96	0	4.3	A			0	3.87	24.01	2.72	C	E	
							0	2.6	25.35	3.17	C	E	
							0	2.29	25.93	3.27	C	E	D
							13.92	10.55	5.99	0	C	A	G
							12.8	9.76	7.44	0	C	G	
							10.26	9.21	9.71	0	C	G	
							7.7	8.83	12.33	0	C	G	
A	Na ₂ SO ₄						4.57	8.73	15.27	0	C	G	
B	Na ₂ SO ₄ ·10H ₂ O						2.5	8.71	17.62	0	C	G	
C	NaCl						0	6.76	20.87	1.98	C	E	G
D	MgSO ₄ ·6H ₂ O						0	2.29	25.93	3.27	C	E	D
E	MgSO ₄ ·7H ₂ O						0	0.4	26.05	4.5	E	D	
F	MgCl ₂ ·6H ₂ O						0	0	25.99	4.75	E	D	
G	Na ₂ SO ₄ ·MgSO ₄ ·4H ₂ O						0.45	0	33.27	3.96	C	D	F
							0.34	0	35.45	0	C	F	
							0	0	33.29	3.9	F	D	

10 Crystallization

The formation of crystals in a solution takes place if the degree of saturation, the saturation index, is sufficiently high. Crystals can be in equilibrium with a saturated solution. If crystals are present in a supersaturated solution, the crystals will grow. If no crystals are present initially, crystals will not form spontaneously in a slightly supersaturated solution. A certain degree of supersaturation is required in order to overcome the Gibbs energy change associated with forming a particle in a solution.

10.1 Supersaturation

Supersaturation is the driving force of crystallization. The degree of saturation necessary to initiate a crystallization process can be produced by cooling, by heating, by evaporating solvent, or by the addition of a salting out agent. A salting out agent reduces the solubility of another solute. Alcohols will usually have a salting out effect on most electrolytes. A salting out agent can also be another salt. The addition of CaCl_2 or MgCl_2 to a saturated NaCl solution will for example cause most of the NaCl to precipitate.

Modern industrial crystallizers often use adiabatic evaporation to produce supersaturation. In adiabatic evaporation, solvent is evaporated adiabatically by vacuum. The heat required for the evaporation causes the temperature of the solvent to drop, and by evaporation the concentration of the solute increases.

The formation of crystals is often, but not always an exothermal process. Adiabatic evaporation consumes the heat released by the crystallization. If the heat of crystallization was not removed from an exothermal crystallization process, the temperature would increase and influence the degree of saturation.

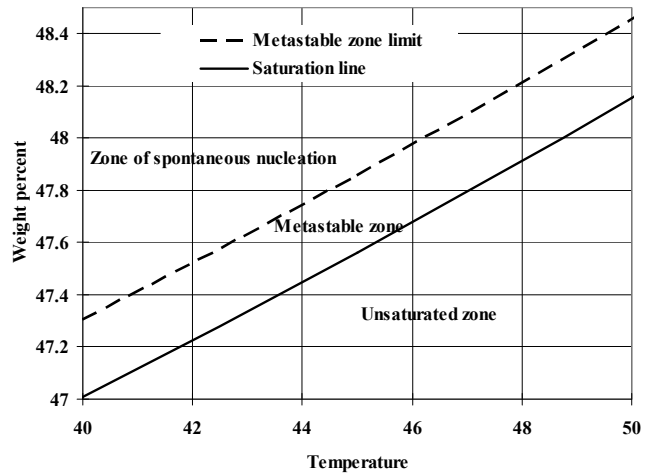


Figure 10.1: Phase diagram showing the metastable zone in which the crystallization process takes place

It is very important to control the degree of saturation in order to achieve the desired result in the crystallization. The crystal growth rate is exponentially dependent on the degree of supersaturation for many systems. The crystal size is often an important attribute of the product. If the crystals grow too fast, liquid inclusions in the crystals are sometimes seen. Large, singular crystals are often desired products. The degree of saturation is often adjusted so that maximum crystal growth is achieved without exceeding the metastable region.

The degree of saturation is measured by the saturation index. It was shown in section 7.2 that equilibrium between a solid salt and a saturated solution can be described by an equation of the type:

$$\frac{-\Delta G^0}{RT} = \sum \nu_i \ln a_i \quad (10.1)$$

ΔG^0 is the increment in Gibbs free energy by the dissolution of a salt in a saturated solution.

The saturation index SI was introduced as the ratio between the activity product and the solubility product:

$$SI = \left(\frac{\prod a_i^{\nu_i}}{\exp\left(\frac{-\Delta G^0}{RT}\right)} \right) \quad (10.2)$$

As it can be seen from equation (10.1), SI is equal to 1 at equilibrium. SI is larger than 1 at supersaturation and less than one in unsaturated solutions.

Equation (10.2) can be written on logarithmic form as:

$$\ln SI = \sum \nu_i \ln a_i + \frac{\Delta G^0}{RT} \quad (10.3)$$

10.2 The Kelvin equation for nucleation

In order for crystal growth to take place, there need to be some nuclei in the solution. Nuclei can be formed by primary nucleation or secondary nucleation. Primary nucleation or homogeneous nucleation is the form of nucleation that takes place in a solution with no crystals present initially. Primary nucleation begins spontaneously when the degree of saturation exceeds the metastable region. The metastable region for a salt is shown in Figure 10.1. Secondary nucleation is the formation of nuclei by attrition or nucleation around impurities. Secondary nucleation is therefore a function of the properties of the solution and of the amount of energy put into the crystallizer as shaft work. It is usually desirable to minimize the amount of secondary nucleation.

The crystallization of a salt in a supersaturated solution starts by the formation of nuclei. Some nuclei have a size less than the critical size and their chance of growing is small. Nuclei larger than the critical size can continue to grow. Here we consider the equilibrium between a nucleus with a certain size and its constituent ions, a metastable equilibrium. The process written for potassium sulfate is:



By forming a spherical nucleus of radius r , additional energy is required due to interfacial

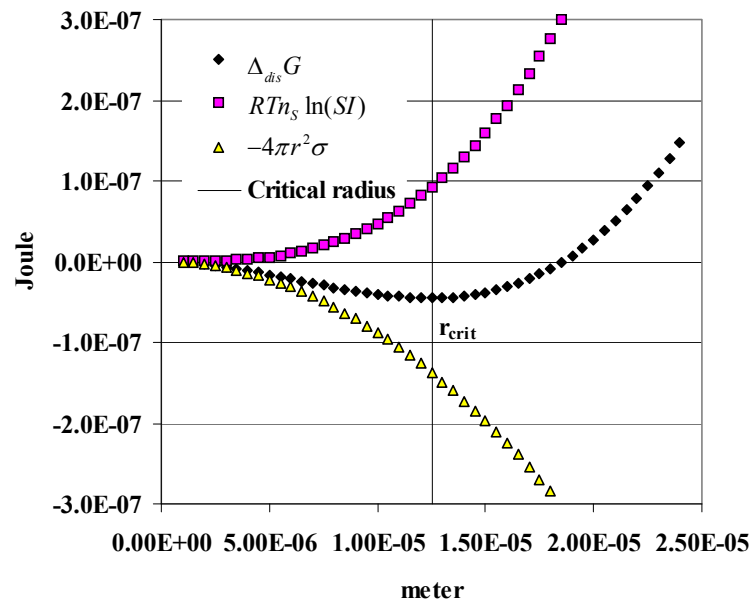


Figure 10.2: The Gibbs energy change by dissolution of a nucleus. Above a certain size, the Gibbs energy change by dissolution is positive, and the crystal will therefore not dissolve.

tension. The surface area of the nucleus is $4\pi r^2$ and the interfacial tension between nucleus and saturated solvent is σ J/m². The increase in Helmholtz energy by forming the surface is therefore $4\pi r^2\sigma$ J. Assuming an insignificant difference between Helmholtz energy and Gibbs energy, the Helmholtz energy change will be considered equal to the Gibbs energy change.

The volume of the nucleus is $4/3\pi r^3$ cubic meter. The molar volume of solid potassium sulfate in the nucleus is $V_{K_2SO_4}$ cubic meter. The number of mol of potassium sulfate in the nucleus is:

$$n_s = \frac{4}{3}\pi r^3 / V_{K_2SO_4} \quad (10.5)$$

It is assumed that the cluster of ions forming the nucleus has the same standard state Gibbs energy as the crystalline salt. The total change in Gibbs energy by the dissolution reaction (10.4) is then given by:

$$\Delta_{dis}G = 2n_s\mu_{K^+} + n_s\mu_{SO_4^{2-}} - n_s\mu_{K_2SO_4(s)}^0 - 4\pi r^2\sigma \quad (10.6)$$

This equation is expanded by introducing the terms for the chemical potentials and the following expression is obtained:

$$\Delta_{dis}G = n_s\Delta G_{K_2SO_4}^0 + n_sRT \ln(a_{K^+}^2 a_{SO_4^{2-}}) - 4\pi r^2\sigma \quad (10.7)$$

According to equation (10.3) this can be written as:

$$\Delta_{dis}G = RTn_s \ln SI - 4\pi r^2\sigma \quad (10.8)$$

A graphical representation of this curve is given in Figure 10.2. In a supersaturated solution, the first term is positive. When the nucleus grows above a certain size, the Gibbs energy change for the dissolution reaction becomes positive. The crystalline form is therefore the most stable under these conditions. At the metastable equilibrium, the derivative of $\Delta_{dis}G$ with respect to n_s has the value zero as the Gibbs energy change for the dissolution goes through its minimum. From the expression for n_s in equation (10.5) the following is obtained:

$$\frac{dn_s}{dr} = \frac{4\pi}{3V_{K_2SO_4}} \frac{dr^3}{dr} = \frac{4\pi r^2}{V_{K_2SO_4}} \quad (10.9)$$

This is used for calculating the nucleus size derivative of the dissolution Gibbs energy:

$$\begin{aligned} \frac{d(\Delta_{dis}G)}{dn_s} &= RT \ln SI - 4\pi\sigma \frac{dr^2}{dn_s} \\ &= RT \ln SI - \frac{4\pi\sigma V_{K_2SO_4}}{4\pi r^2} \frac{dr^2}{dr} \\ &= RT \ln SI - \frac{2\sigma V_{K_2SO_4}}{r} \end{aligned} \quad (10.10)$$

The metastable equilibrium occurs when the derivative in equation (10.10) is equal to zero. At this nucleus size, the radius of the nucleus is the critical radius, r_{crit} . The resulting equation is the Kelvin equation for the formation of crystal nuclei in a solution:

$$\frac{2\sigma V_{K_2SO_4}}{RT r_{crit}} = \ln SI \quad (10.11)$$

The Kelvin equation was originally derived for the calculation of the vapor pressure of a liquid when it is dispersed as droplets of a certain radius [89]. Compared to the original Kelvin equation, in equation (10.11) $\ln SI$ replaces $\ln(p/p^*)$, where p^* is the vapor pressure of the liquid when it is not dispersed as droplets and p is the vapor pressure of the liquid when it is dispersed. As an analogy with the original Kelvin equation, the Kelvin equation for the formation of crystal nuclei in a solution enables us to calculate the activity product of a salt in the liquid outside a spherical, solid nucleus of a certain radius. The main use of this equation however is for the calculation of a theoretical expression for the activation energy for the formation of a nucleus of the critical size.

10.3 Activation energy for crystal formation

By using the value of the critical radius of a spherical crystal in equation (10.8) and replacing n_s by the expression in equation (10.5), the critical Gibbs energy change for forming a nucleus of the critical size can be evaluated:

$$\begin{aligned}
 \Delta_{dis} G^{crit} &= RTn_s \ln SI - 4\pi r^2 \sigma = \frac{4\pi}{3V_{K_2SO_4}} r_{crit}^3 RT \ln SI - 4\pi \sigma r_{crit}^2 \\
 &= \frac{4\pi}{3V_{K_2SO_4}} \left(\frac{2\sigma V_{K_2SO_4}}{RT \ln SI} \right)^3 RT \ln SI - 4\pi \sigma \left(\frac{2\sigma V_{K_2SO_4}}{RT \ln SI} \right)^2 \\
 &= \frac{4\pi}{3V_{K_2SO_4}} \frac{8\sigma^3 V_{K_2SO_4}^3}{R^2 T^2 (\ln SI)^3} \ln SI - 4\pi \sigma \frac{4\sigma^2 V_{K_2SO_4}^2}{R^2 T^2 (\ln SI)^2} \\
 &= -\frac{16\pi \sigma^3 V_{K_2SO_4}^2}{3(RT \ln SI)^2}
 \end{aligned} \tag{10.12}$$

This is the critical Gibbs energy change for the dissolution of one nucleus consisting of n_s mol potassium sulfate. The critical Gibbs energy change for the formation of one nucleus $\Delta_{form} G^{crit}$ has the corresponding positive value. This positive Gibbs energy change can be considered as the activation energy for forming a spherical nucleus of the critical size.

10.4 Primary nucleation rate

Based on the calculated activation energy, the primary nucleation rate can be described by a Boltzmann (or Arrhenius) type equation:

$$B^0 = C \exp\left(-\frac{\Delta_{form} G^{crit}}{kT}\right) = C \exp\left(-\frac{N_A 16\pi \sigma^3 V_{K_2SO_4}^2}{3(RT)^3 (\ln SI)^2}\right) \tag{10.13}$$

C is the so-called pre-exponential factor. The activation energy in Joule per nucleus is divided by the Boltzmann factor $k = R/N_A$ J/K and the Kelvin temperature. The exponential factor has a value between zero and one. This factor is an expression for the probability of reaching the activation energy. Obviously, primary nucleation is an exponential function of the degree of saturation and of temperature. A high saturation index and a high temperature increase the probability of reaching the activation energy.

89 Thomson, Sir William (later Lord Kelvin), Phil. Mag. 42(1871)448

11 Fractional crystallization

Fractional crystallization is the most common method for separating a pure salt from a solution of salts. By this method, the salts are crystallizing as pure salts, but it is usually not possible to separate the pure salts completely from the mother liquid. Mother liquor is the name used for a saturated solution from which crystallization has taken place. The pure phases of crystalline salts will therefore be mixed with some mass percents of saturated solution. After the crystals are taken out from the crystallizer, they are therefore usually centrifuged or filtered to separate them from mother liquor. Afterwards, the crystals can be washed with water in order to remove any mother liquor adsorbed on the surfaces of the crystals.

Fractional crystallization will first be illustrated by an example of separation in a ternary system. The temperature/composition dependence of the precipitation from a ternary system can be seen from a temperature/two salt saturation point diagram like the one shown in Figure 11.1. In the NaCl-Na₂SO₄-H₂O system shown in Figure 11.1 three different phases can appear in the temperature range shown in the diagram. At lower temperatures hydrohalite, NaCl·2H₂O and ice will appear.

The process path for separating a mixture of sodium sulfate and sodium chloride into one solid phase of glauber's salt (Na₂SO₄·10H₂O) and one solid phase of sodium chloride (NaCl) is illustrated in Figure 11.1. The feed mixture consists of water and equal molar amounts of NaCl and Na₂SO₄. The line a-b represents the precipitation of glauber's salt caused by isothermal evaporation, b-c represents the heating of the solution from 3 to 43°C. By heating the solution, the precipitation field changes from glauber's salt to sodium chloride. The

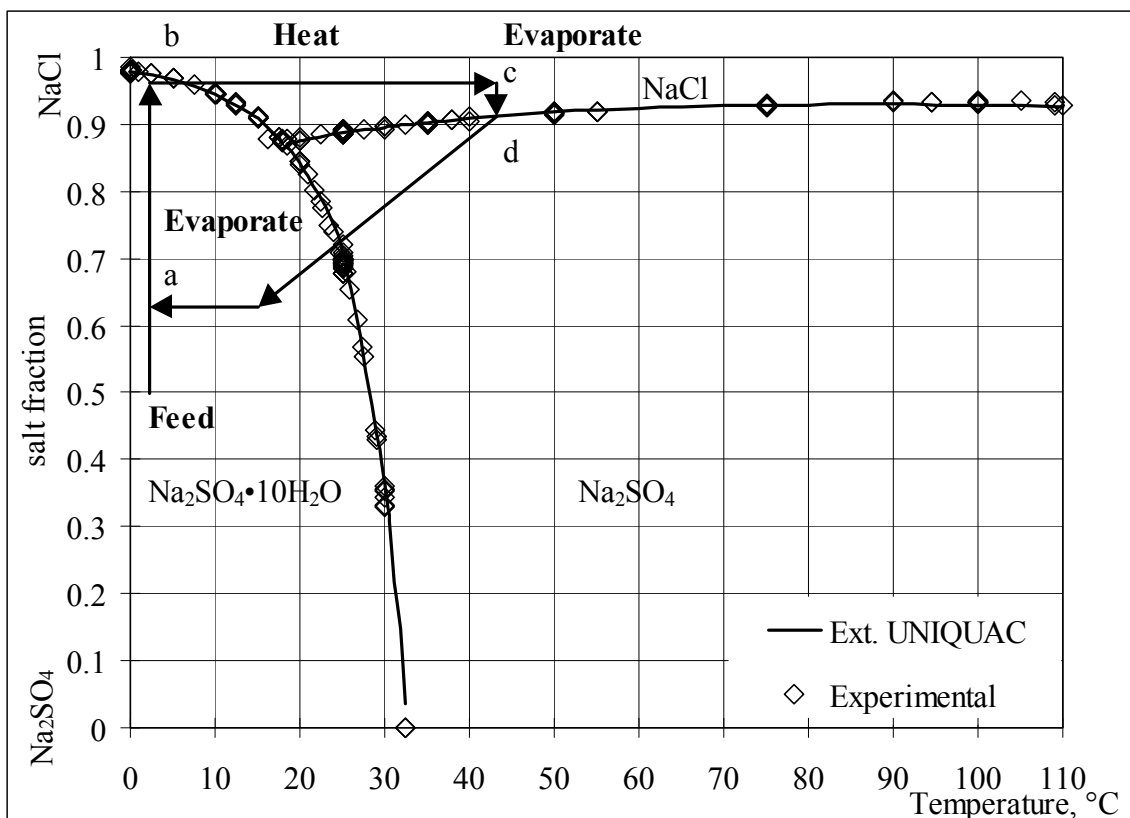


Figure 11.1: Process path for the fractional crystallization of sodium chloride (NaCl) and glauber's salt (Na₂SO₄·10H₂O)

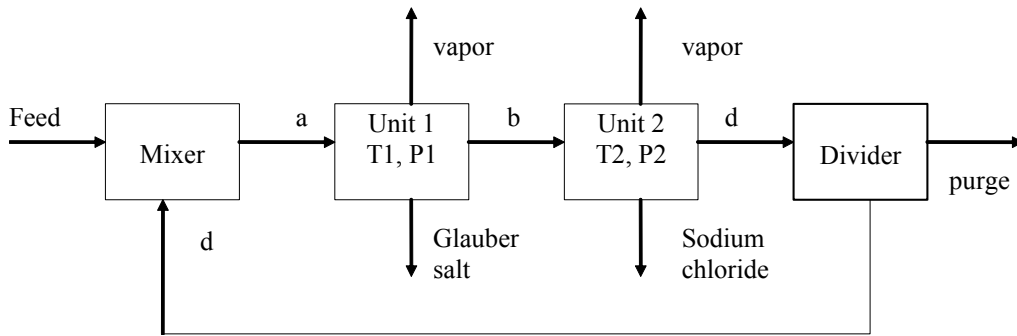


Figure 11.2: Outline of equipment for performing a fractional crystallization.

precipitation of sodium chloride takes place along the line c-d, caused by isothermal evaporation. The line d-a represents the mixing of the NaCl-saturated solution from d with fresh feed and a cooling to 3°C.

Fractional crystallizations like the one described above and illustrated in Figure 11.1 can be performed in a system consisting of two crystallizers in series as outlined in Figure 11.2. The cooling and the isothermal evaporation stage are often combined to an evaporative cooling stage.

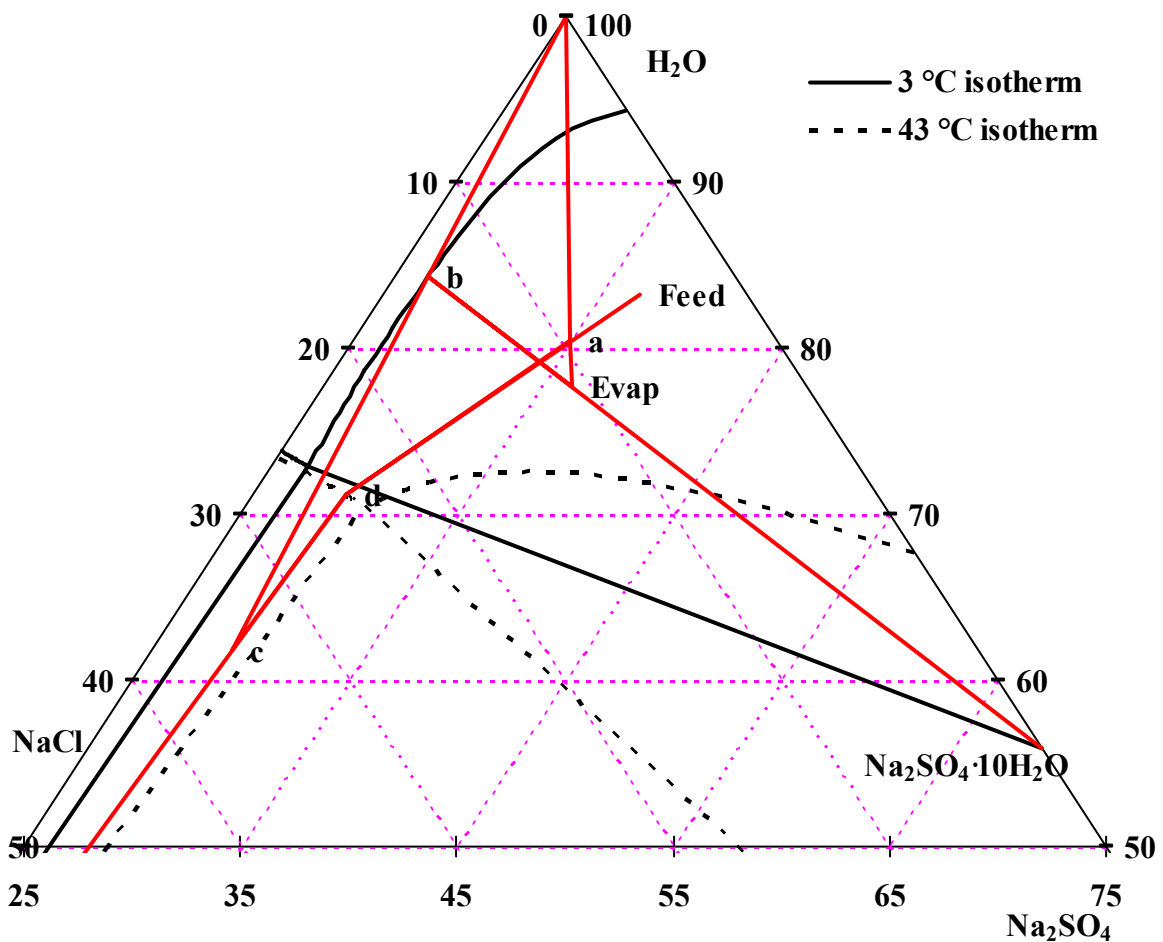


Figure 11.3: Solubility isotherms with operating lines for the fractional crystallization process for separating glauber's salt from sodium chloride.

The operating lines of this fractional crystallization process are plotted in the two relevant isotherms, 3 °C and 43 °C in Figure 11.3. Note that only the upper part of the triangular diagram is shown in Figure 11.3. The composition of NaCl and Na₂SO₄ are outside the diagram. The points in the isotherms are marked with the same letters that were used in Figure 11.1.

The point marked “Feed” represents the composition of the feed stream. The feed stream is mixed with the mother liquor from the NaCl crystallization, marked “d”. The composition of the mixed stream is on the straight line between “Feed” and “d”, marked “a”. By evaporation of water from the stream marked “a” the composition of the stream moves down along a straight line going through the point representing pure water and the point marked “a”. The composition of the stream after the evaporation is marked “Evap”. This point is clearly inside the field supersaturated with glauher’s salt at 3 °C, but in the un-saturated field according to the 43 °C isotherm. Next, glauher’s salt (Na₂SO₄·10H₂O) precipitates from the solution marked “Evap”. The precipitation takes place along a straight line going through the point marked “Evap” and the point representing the composition of solid glauher’s salt. The mother liquor from the glauher’s salt precipitation has the composition marked “b” in the diagram. The point “b” is on the glauher’s salt branch of the 3 °C isotherm.

After the glauher’s salt precipitation, the stream is heated to 43 °C and water is evaporated from the solution. The evaporation follows a straight line going through the point representing pure water, down to the point marked “c”. The composition of the stream at point “c” is supersaturated with NaCl at 43 °C. NaCl precipitates from this solution along a line going through the point in the diagram representing NaCl(s) and the point “c”. This line has to end in “d” on the NaCl branch of the 43 °C isotherm. Point “d” represents the mother

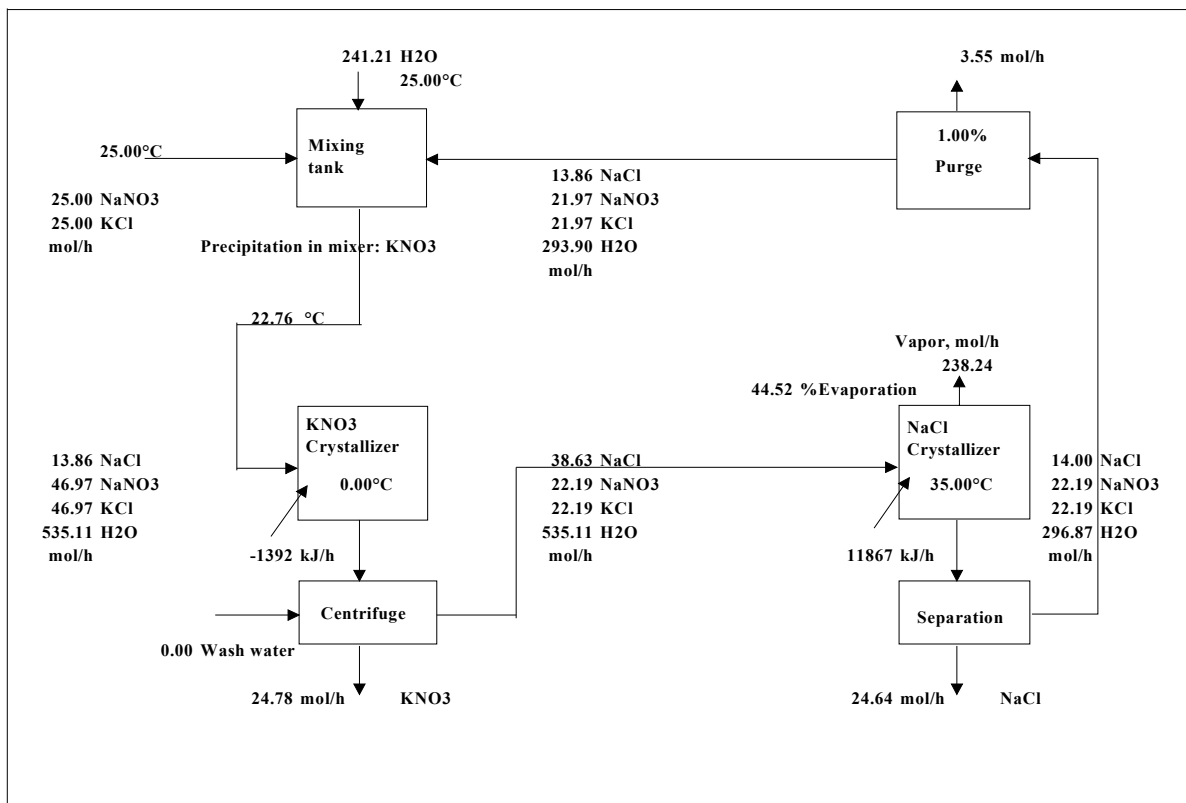


Figure 11.4: Production of KNO₃ from NaNO₃ and KCl, design one

liquor from the NaCl crystallization. This mother liquor is mixed with feed stream again to continue the process in steady state.

11.1 Production of KNO_3

Potassium nitrate can be produced by fractional crystallization of mixtures of potassium chloride and sodium nitrate. As a by-product sodium chloride is also produced in the process. Two alternative flowsheet designs of this fractional crystallization process will be discussed here. The process takes place in the quaternary system consisting of $(K^+, Na^+) - (Cl^-, SO_4^{2-}) - H_2O$. In both flowsheet designs, potassium nitrate is precipitating at 0 °C and sodium chloride at 35 °C.

In the first flowsheet design, shown in Figure 11.4, fresh feed is mixed with water and with mother liquor from the sodium chloride crystallization. The mixture is cooled to 0 °C and potassium nitrate precipitates. The mother liquor from the potassium nitrate precipitation is transferred to the sodium chloride crystallizer where it is heated to 35 °C and water is evaporated. Sodium chloride precipitates and the mother liquor from this crystallizer is again mixed with fresh feed and water.

In the second flowsheet design, shown in Figure 11.6, fresh feed is mixed with mother liquor from the potassium nitrate crystallizer. The mixture is heated to 35 °C and water is

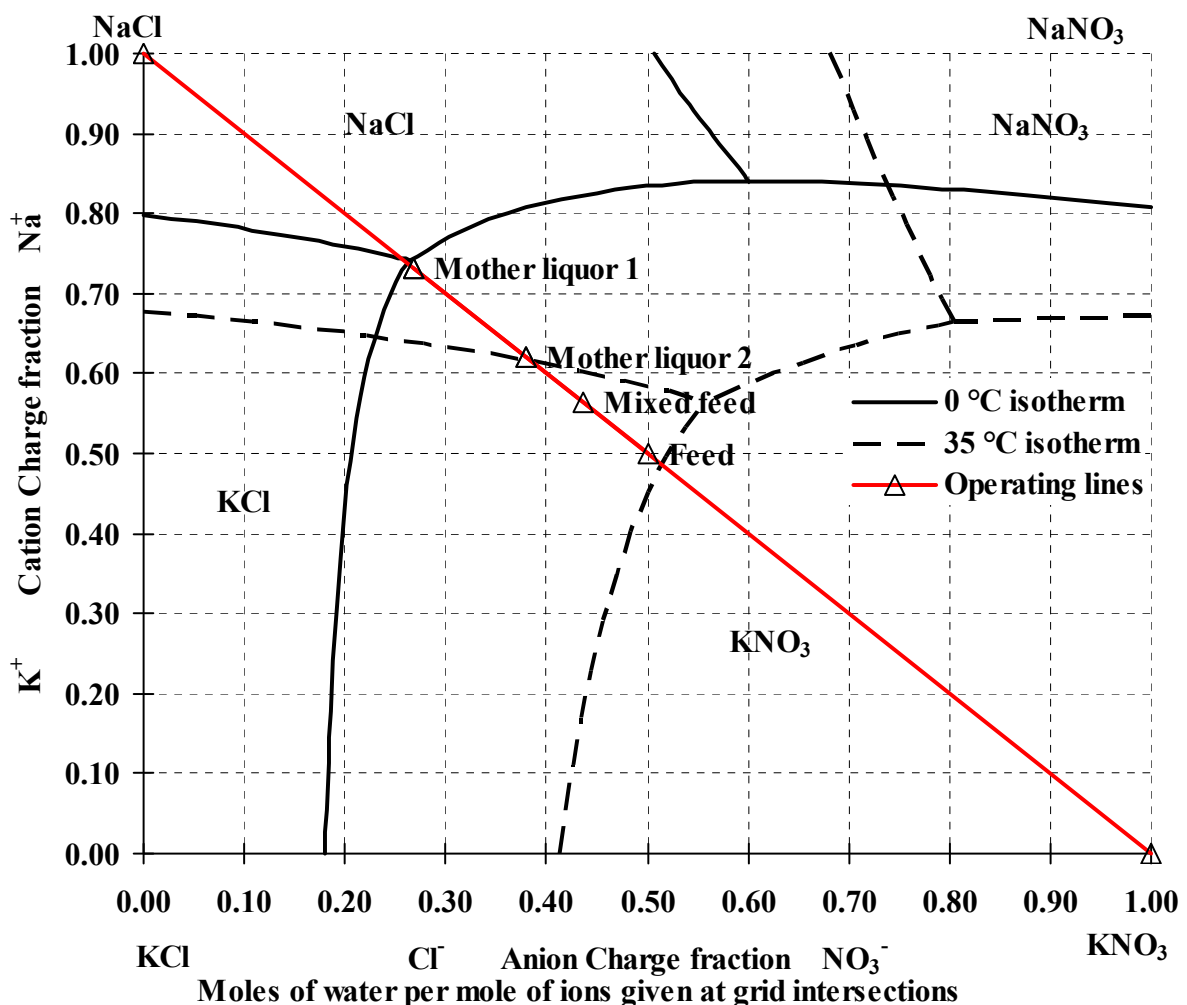


Figure 11.5: Operating lines for potassium nitrate production, design 1

evaporated in the sodium chloride crystallizer. The mother liquor from the sodium chloride crystallizer is mixed with water and led to the potassium nitrate crystallizer. In the potassium nitrate crystallizer, the mixture is cooled and potassium nitrate precipitates. The mother liquor from the potassium nitrate crystallizer is again mixed with fresh feed in the steady state process.

The operating lines for the flowsheet design in Figure 11.4 are shown in Figure 11.5. The feed stream with a composition located at (0.5, 0.5) is mixed with “Mother liquor 2” from the sodium chloride crystallization to form the “Mixed feed”. The mixed feed is cooled to 0 °C. From Figure 11.5 it can be seen that the mixed feed is in the KCl saturation field in the 35 °C isotherm. In the 0 °C isotherm, the mixed feed is in the KNO₃ saturation field. KNO₃ crystallizes from the solution along the operating line going from “Mother liquor 1” to KNO₃. The composition of the point “Mother liquor 1” is inside the KNO₃ saturation field in the 0 °C isotherm. Only KNO₃ will therefore crystallize in this stage.

Mother liquor 1 is heated to 35 °C and water is evaporated in the NaCl crystallizer. The composition of “Mother liquor 1” is inside the NaCl saturation field in the 35 °C isotherm. By the evaporation, water evaporates and NaCl crystallizes along the operating line going from “Mother liquor 2” to NaCl in Figure 11.5. “Mother liquor 2” is inside the NaCl saturation field in the 35 °C isotherm ensuring that only NaCl crystallizes in this stage.

The operating lines are all on the same straight line in this example. If the feed for this process contained a surplus of NaNO₃ compared to the equivalent amount of KCl, the operating lines for the mixing of the feed with “Mother liquor 2” would have a different slope than the diagonal. But this surplus of NaNO₃ would have to leave the process in the purge stream because there would not be enough potassium ions to precipitate the nitrate ions as

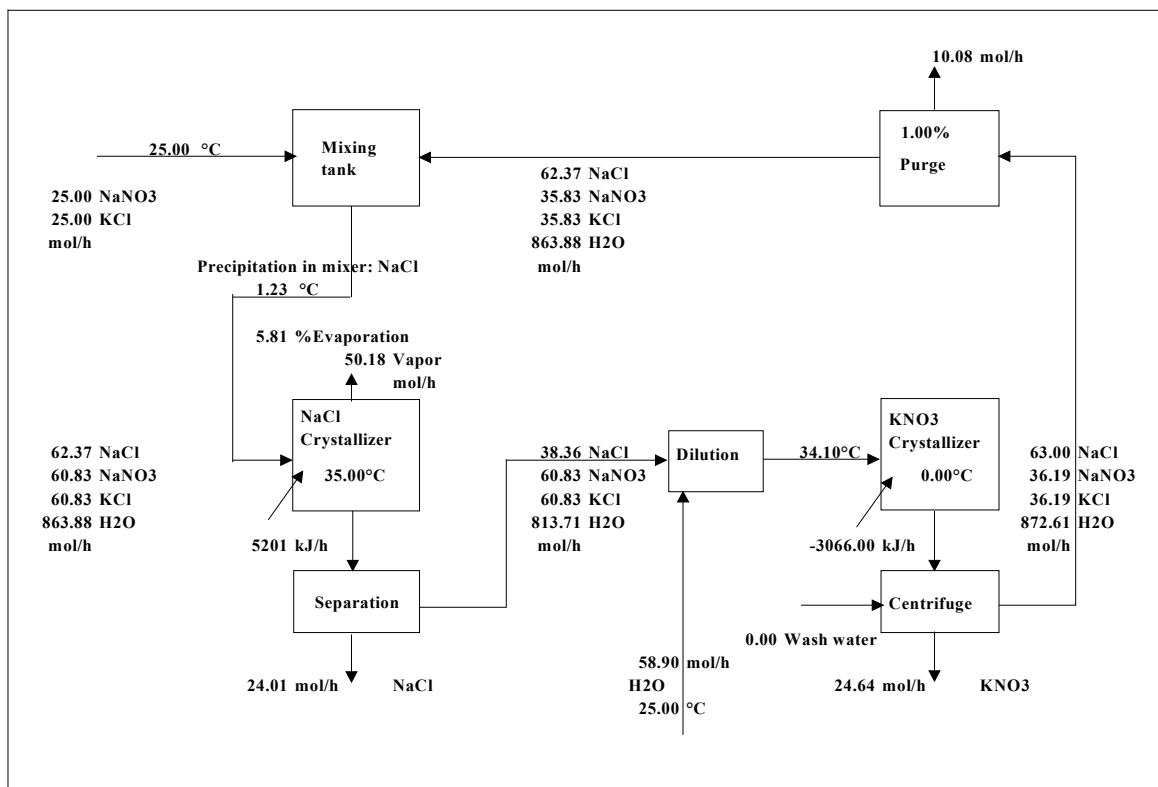


Figure 11.6: Production of KNO₃ from NaNO₃ and KCl, design two

KNO₃.

If the water content of the solutions in this process could be seen in Figure 11.5, it would be seen that only the projections of the operating lines form a straight line. The operating lines themselves are connecting points with varying water content and are therefore separate lines in the diagram. The projections of the operating lines for the production of KNO₃ according to design two follow a pattern similar to the operating lines of design one. If the water content of the solutions were visible in the diagram, there would be a clear difference between the two sets of operating lines.

11.2 Optimization of fractional crystallization processes

Both flowsheet designs were simulated and optimized with software that uses the Extended UNIQUAC thermodynamic model for calculating the excess properties and phase behavior of electrolyte solutions. The objective of the optimization was to maximize the yield of KNO₃. The design variables were the amount of water added to the system, the percentage of water evaporated in the NaCl crystallizer, and the percentage of recirculation stream purged.

Two constraints were added to ensure a yield of pure KNO₃ and pure NaCl. These constraints were formulated as a maximum value (0.9) of the secondary saturation indices in the mother liquor from the two crystallizers. In the mother liquor, the saturation index of the salt that precipitated is equal to one. The secondary saturation index of the mother liquor is the highest saturation index of the remaining salts in the mother liquor.

The results of the optimizations are displayed in Figure 11.4 and Figure 11.6. The yield of potassium nitrate is approximately the same in the two designs. The energy consumption for heating and cooling, however, is significantly different. Compared to design two, design one requires more than twice as much heating (11867 kJ h⁻¹ as opposed to 5201 kJ h⁻¹) but only a little more than half the cooling (1392 kJ h⁻¹ as opposed to 3066 kJ h⁻¹). Also the size of the

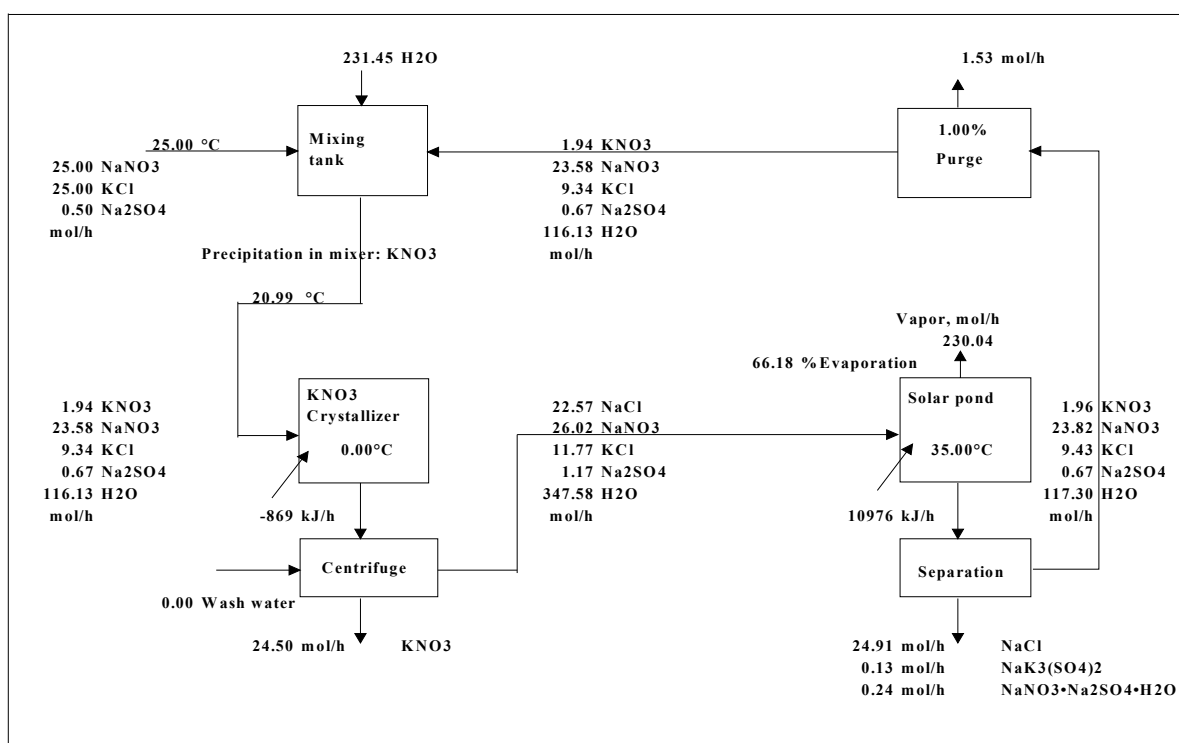


Figure 11.7: Production of KNO₃ from NaNO₃, KCl, and Na₂SO₄, design one

recirculation stream in design one is less than half of the recirculation stream in design two. If the evaporation is performed in solar evaporation ponds as indicated, the heat consumption may be of minor importance and design one can be regarded as the most efficient.

In both optimized designs, the adiabatic flash performed in order to calculate the temperature of the mixed stream from the mixing tank indicates that precipitation begins in the mixing tank. It is therefore necessary to either heat the mixing tank or to perform the mixing in the crystallizer.

The lower boundary for the percentage of recirculation stream purged was set to 1.00%. As it appears from Figure 11.4 and Figure 11.6, this lower boundary was reached in the optimal solutions to both designs. If the feed did not contain equivalent amounts of sodium nitrate and potassium chloride, the purge stream would have been larger.

The raw material for the KNO_3 production may contain some sodium sulphate. Figure 11.7 shows what effect a small content of sodium sulphate will have on design one. Also here the maximum allowable secondary saturation index in the mother liquor from the KNO_3 crystallizer was set to 0.90 while no constraints were put on the mother liquor from the chloride/sulphate precipitation. The flowsheet was optimized for the maximum yield of KNO_3 .

As it appears from Figure 11.7, the same yield of KNO_3 can be obtained as in the system without Na_2SO_4 even with a lower cooling capacity. KNO_3 however is the only pure product obtained from the process. A complete separation of the feed into three pure products would require an additional crystallization process.

If a feed containing Na_2SO_4 was used in connection with design two, the amount of water added between the two crystallizers would be about ten times as large as the amount used in Figure 11.7, the recirculation stream would become larger and the amount of heat required for evaporating water would grow considerably. Thus, design one is clearly the most advantageous if the feed contains Na_2SO_4 .

11.3 Simulation of K_2SO_4 production process

When double salts are involved, fractional crystallization processes become more complex and require more crystallization stages. The process for the production of K_2SO_4 and NaCl from Na_2SO_4 and KCl is one such example. The phase diagram for the system is shown in Figure 11.8. The formation of the double salt glaserite $\text{NaK}_3(\text{SO}_4)_2$ makes a simple separation process impossible. The general method to achieve the separation is to divide the phase diagram into sub-systems. In the first sub-system, the double salt is produced. Next, the desired salt can be produced by mixing the double salt with another salt.

In the phase diagram (30°C), Figure 11.8, the fields have been marked with the corresponding salts. Circles are marking the points in the diagram corresponding to the composition of the solid phases.

The two sub-systems, that are used in order to bring about the fractional crystallization, have been separated by the dashed line.

The first sub-system is the upper part of the diagram. The mixing of KCl and Na_2SO_4 leads to a composition located on a straight line between the points representing the compositions of the solid salts. This line - which is not marked in Figure 11.8 - passes through the KCl field, the very large $\text{NaK}_3(\text{SO}_4)_2$ field, and the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ field.

The second subsystem, is the triangle below the dashed line. In this second system, the mixing of KCl and $\text{NaK}_3(\text{SO}_4)_2$ will result in a composition located on the dashed line in Figure 11.8. By supersaturation of this mixture, K_2SO_4 will precipitate.

A flow sheet for the production of K_2SO_4 and NaCl from Na_2SO_4 and KCl is shown in Figure 11.9. In the crystallizer marked 'Glaserite reaction', Na_2SO_4 and KCl are mixed with a recirculation stream. Cooling of the crystallizer causes

glaserite, $\text{NaK}_3(\text{SO}_4)_2$ to precipitate. The mother liquor from this crystallizer is further cooled in the 'Glauber salt' crystallizer, causing glauber's salt to precipitate. Next the mother liquor from this crystallizer is heated in the 'Sodium chloride' crystallizer, and water is evaporated. This causes sodium chloride to precipitate, and the remaining mother liquor is returned to the first crystallizer. This constitutes the Na_2SO_4 - NaCl - KCl - $\text{NaK}_3(\text{SO}_4)_2$ sub-system.

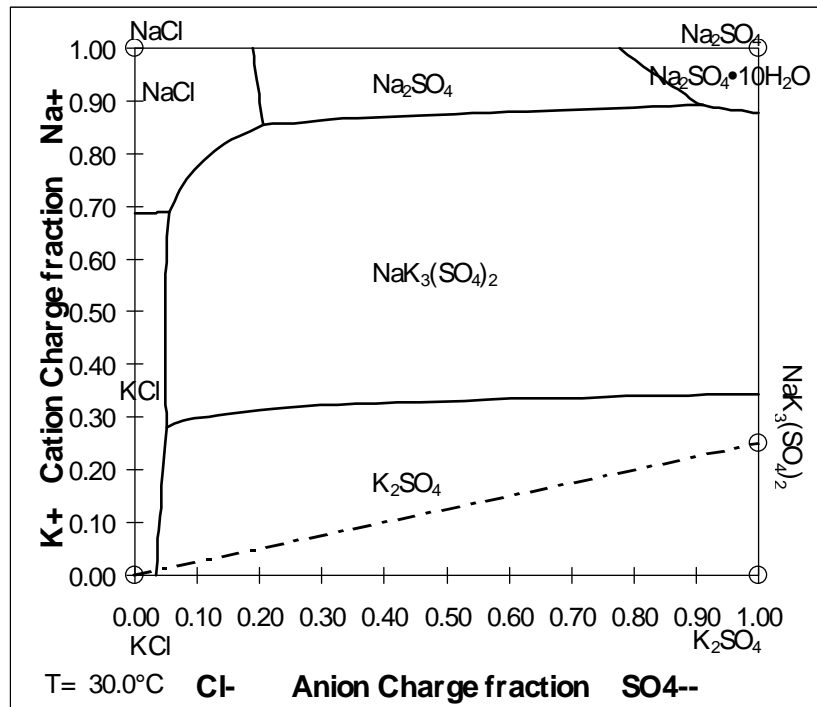


Figure 11.8: Jänecke projection of the phase diagram for the system considered in example 3. The dashed line divides the phase diagram into two sub-systems.

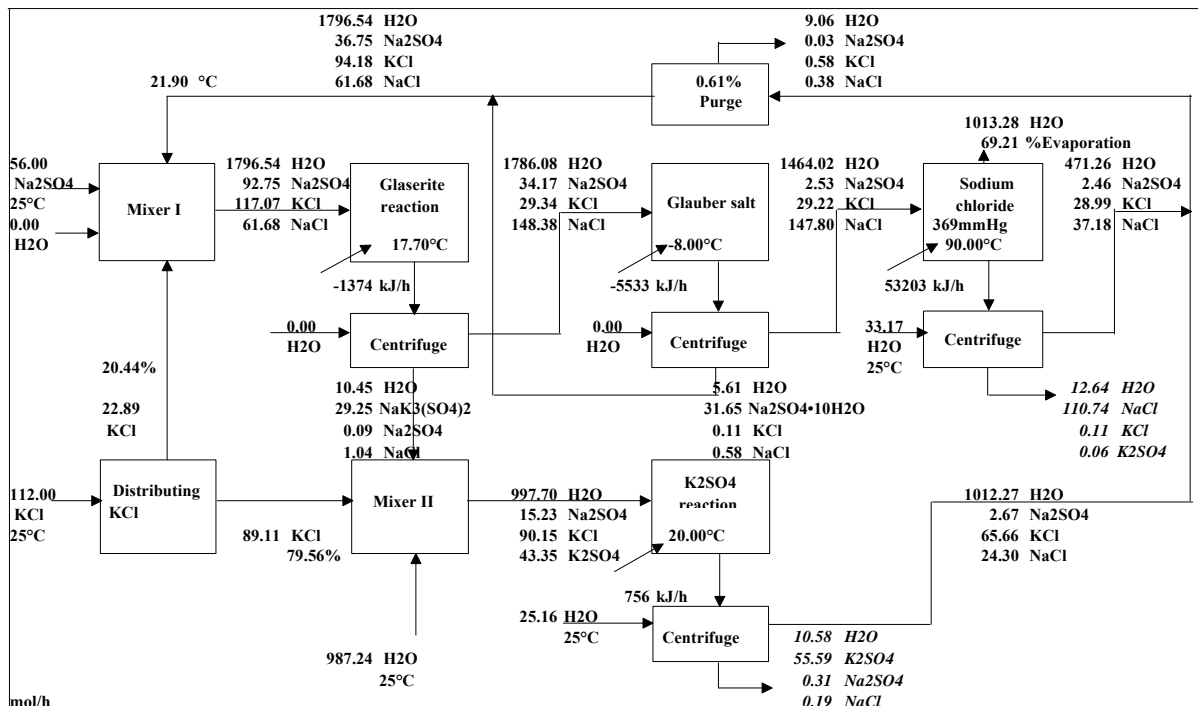


Figure 11.9: Flow sheet for a fractional crystallization process, producing potassium sulfate and sodium chloride from potassium chloride and sodium sulphate.

In the second sub-system potassium chloride and glaserite are mixed, potassium sulfate precipitates and the mother liquor is returned and mixed with fresh feed in the first sub-system.

The operating lines for the “Glaserite reaction” from Figure 11.9 are shown in Figure 11.10. The recirculation stream is mixed from the mother liquor of the glauber’s salt crystallizer, the sodium chloride crystallizer and the potassium sulfate crystallizer. This recirculation stream is mixed with fresh feed to give a stream of the composition “Glaserite feed” in Figure 11.10. At 17.7 °C, the composition of this stream corresponds to the precipitation of glaserite. The operating line of the glaserite crystallization go from the point marked $\text{NaK}_3(\text{SO}_4)_2$ in Figure 11.10 to the mother liquor composition marked “Glaserite ML”. The point marked $\text{NaK}_3(\text{SO}_4)_2$ is located outside of the glaserite precipitation field indicating that solid glaserite can not be in equilibrium with a solution of the same ionic composition as the salt at this temperature.

The composition of the mother liquor from the glaserite precipitation is outside the glaserite field, which means that a small amount of sodium sulphate is also precipitating in this crystallizer. It is not important to produce glaserite as a pure salt because glaserite is only an

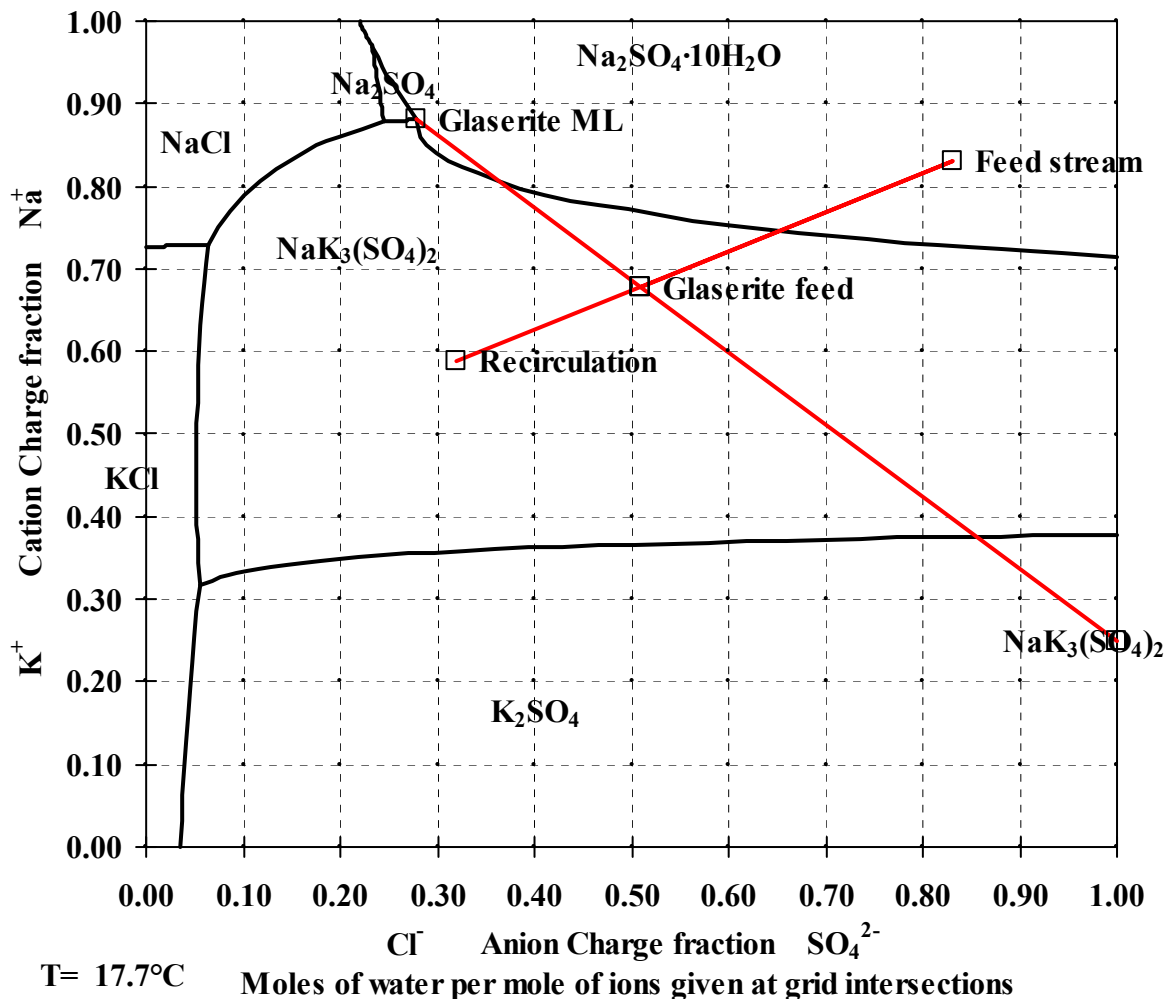


Figure 11.10: Operating lines for the “Glaserite reaction” in Figure 11.9 plotted with the 17.7 °C isotherm.

intermediate product.

The mother liquor from the glaserite reaction contains a large amount of chloride from the potassium chloride added to the process. The goal of the process is to produce potassium sulfate and sodium chloride from sodium sulfate and potassium chloride. Sodium chloride can not be produced directly from the mother liquor from the glaserite reaction. Instead this mother liquor is cooled, whereby the solution becomes supersaturated with glauher's salt. Glauber's salt is produced in a separate crystallizer. The mother liquor from the glauher's salt crystallizer has a composition that makes it possible to produce sodium chloride from it at high temperature, by evaporation of water.

The produced, impure glaserite is used in the second subsystem. In this subsystem, glaserite is mixed with potassium chloride to produce the final product, potassium sulfate. The remaining mother liquor is sent back to the glaserite reaction.